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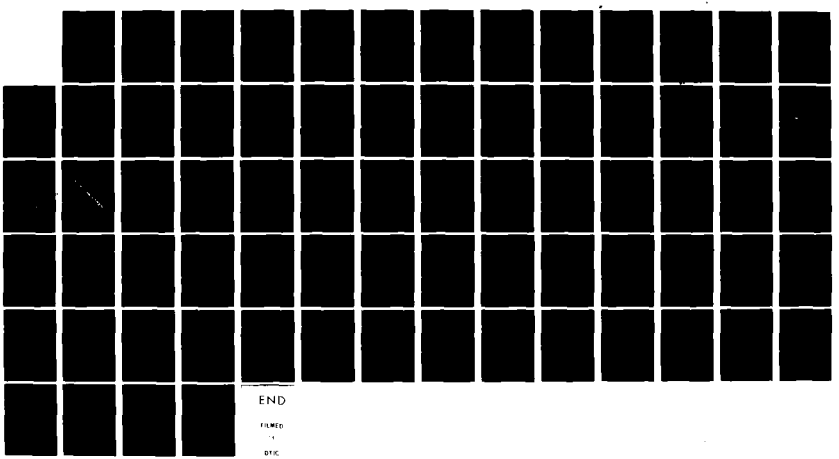

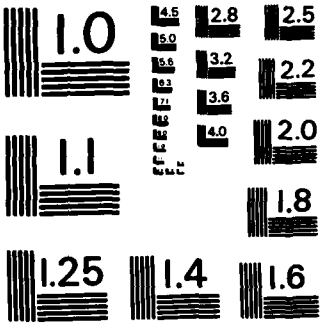

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ABSORPTION OF IR RADIATION BY H_2O AND OTHER ATMOSPHERIC SPECIES: I. DIPOLE AUTOCORRELATION FUNCTION FOR FAR-WING PRESSURE BROADENING. II. UPDATING THE AFGL LINE PARAMETERS ATLAS FOR ASYMMETRIC ROTOR MOLECULES.

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March 1981

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In the first section of this report we describe a new approach for calculating the dipole autocorrelation function for molecular pressure broadening; the method satisfies the Fluctuation-Dissipation Theorem (FDT) on a microscopic basis. This is an important requirement for calculating far-wing molecular absorption. Tasks remaining for numerical implementation of the theory are also outlined and discussed.

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20. ABSTRACT

The second section describes procedures which have been developed to update the AFGL Line Parameters Compilation. The updating subroutines are documented, and a list of fourteen H_2O bands to which the procedure has been applied is given. These bands have been incorporated into the 1980 Edition of the AFGL Atlas.

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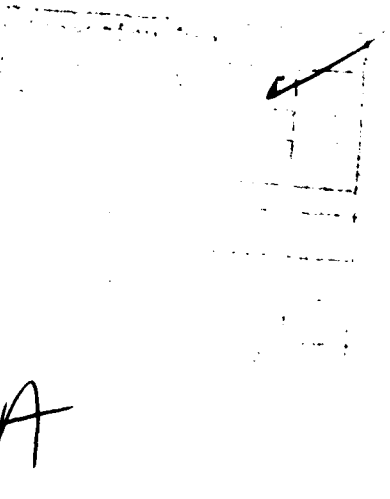

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1.0 INTRODUCTION

The work presented in this report has been directed in two rather different areas, which are discussed separately in Sections 2.0 and 3.0.

In Section 2.0 we describe a new method of computing the dipole autocorrelation function for molecular pressure broadening. We believe that numerical implementation of this approach should yield reliable estimates of far-wing absorption by H_2O and other molecular species.

In Section 3.0 we document the software which has been developed for updating the AFGL Line Parameters Compilation[1/] for asymmetric rotor molecules. In Section 3.0 we describe the function of the various editing, sorting, and comparison subroutines which are used in the updating procedure. A listing of the various H_2O bands for which the procedure has already been applied is provided. These updated bands have all been incorporated into the 1980 Edition of the AFGL Line Parameters Compilation.

2.0 A NEW APPROACH TO THE DIPOLE AUTOCORRELATION FUNCTION FOR MOLECULAR PRESSURE BROADENING

The work reported in this section has benefited greatly through active participation by S. A. Clough of Air Force Geophysics Laboratory, and by R. H. Tipping of the University of Nebraska at Omaha.

The absorption coefficient of a gas may be computed as the Fourier transform of the dipole autocorrelation function[2]

$$\phi(t) = \langle \vec{\mu}(0) \cdot \vec{\mu}(t) \rangle \tag{1}$$

where $\vec{\mu}(t) = e^{\frac{iHt}{\hbar}} \vec{\mu}\, e^{-\frac{iHt}{\hbar}}$ is the Heisenberg dipole moment operator, and where the average denotes a statistical average over the canonical thermal equilibrium density matrix

$$\rho(H) = \exp(-\beta H)/\mathrm{Tr}\{e^{-\beta H}\}. \tag{2}$$

The absorption coefficient can then be expressed in three equivalent forms:

$$\alpha(\omega) = \frac{4\pi^2\omega}{3c\hbar} n_{rad.}\, X''(\omega), \tag{3}$$

with

$$X''(\omega) = \tanh\left(\frac{\beta\hbar\omega}{2}\right) \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{-i\omega t} [\phi(t) + \phi(-t)], \tag{4a}$$

$$= (1 - e^{-\beta\hbar\omega}) \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{-i\omega t} \phi(t), \tag{4b}$$

$$= \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{-i\omega t} [\phi(t) - \phi(-t)]. \tag{4c}$$

The equivalence of the above three formulas is contained in the time-domain statement of the Fluctuation-Dissipation Theorem[3] (FDT),

$$\phi(-t) = \phi(t + i\beta\hbar), \tag{5}$$

which follows from cyclic invariance in expression (1) for the dipole correlation function.

The statement of the FDT in the frequency domain is

$$\phi(-\omega) = e^{-\beta\hbar\omega}\, \phi(\omega), \tag{6}$$

where

$$\phi(\pm\omega) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\; e^{-i\omega t}\, \phi(\pm t). \tag{7}$$

In near-wing pressure broadening theory, it is not terribly crucial that the FDT be satisfied in any approximate theory. This is not the case in considering far-wing absorption, as the following simple example will illustrate. In particular, if one evaluates formulas (4a) - (4c) using the well-known impact approximation,[4] one obtains the results

$$X''(\omega) = \tanh\left(\frac{\beta\hbar\omega}{2}\right) \sum_{if} \rho_i\, |\langle i||\mu||f\rangle|^2 \cdot \frac{1}{\pi}\left[\frac{\Gamma}{(\omega-\omega_{fi})^2+\Gamma^2} + \frac{\Gamma}{(\omega+\omega_{fi})^2+\Gamma^2}\right], \tag{8a}$$

$$X''(\omega) = (1 - e^{-\beta\hbar\omega}) \sum_{if} \rho_i\, |\langle i||\mu||f\rangle|^2 \cdot \frac{1}{\pi} \frac{\Gamma}{(\omega-\omega_{fi})^2+\Gamma^2}, \tag{8b}$$

$$X''(\omega) = \sum_{if} \rho_i\, |\langle i||\mu||f\rangle|^2 \cdot \frac{1}{\pi}\left[\frac{\Gamma}{(\omega-\omega_{fi})^2+\Gamma^2} - \frac{\Gamma}{(\omega+\omega_{fi})^2+\Gamma^2}\right]. \tag{8c}$$

In the extreme far-wings ($\omega >> \omega_{fi}$ for all strong lines), these three formulas predict very different results for the estimated absorption. Thus we view it as crucial that any treatment of far-wing absorption should satisfy the FDT.

In the course of the present contract we have formulated a method of constructing the autocorrelation function in such a way that it satisfies the FDT on a microscopic basis. The approximations of the theory are:

a. The binary collision approximation (this is well-justified in the far wings for atmospheric densities).

b. The uncoupled line approximation (the validity is not easy to assess, however, one might expect line-coupling effects to average out in the far-wing region).

c. Isotropic interactions are treated exactly; anisotropic interactions are treated by second order perturbation theory. This latter approximation might be improved on by making the approximation of ignoring the effects of time-ordering in treating various time-development operators.

A complete derivation of the formalism described above is presented in Appendix A. Here we briefly outline a few of the more relevant results.

Within the uncoupled line and binary collision approximations, we find that the autocorrelation function is given by

$$\phi(t) = \nu \sum_{j_i j_f} \rho(\epsilon_{j_i})(2j_i + 1) \, |\langle j_i||\mu||j_f\rangle|^2 \cdot e^{\frac{i}{\hbar}(\epsilon_{j_f} - \epsilon_{j_i})t} \, C_{if}(t). \tag{9}$$

This result satisfies the FDT provided $C_{fi}(-t) = C_{if}(t+i\beta\hbar)$. For the $C_{if}(t)$ correlation functions, we obtain

$$C_{if}(t) = \exp\{N_p [q_{if}(t) - 1]\} \tag{10}$$

where N_p is the number of perturbers, and with

$$q_{if}(t) = \frac{1}{(2j_i+1)} \sum_{\substack{m_i m_i' \\ m_f m_f' m}} (j_f l m_f m | j_f l j_i m_i) \cdot (j_f l m_f' m | j_f l j_i m_i')$$

$$\cdot \mathrm{Tr}\ \{\rho(\tilde{H}_0)\ \langle j_i m_i' | U(t - i\beta\hbar) | j_i m_i \rangle$$

$$\cdot \langle j_f m_f | U(t)^\dagger | j_f m_f' \rangle\}. \qquad (11)$$

In this expression, the bracketed quantities are Clebsch-Gordon coefficients, and the U's are time-development operators. From Eqs. (9), (10), (11) one can indeed show that the FDT is satisfied, along with the reality condition $C_{if}(t)^* = C_{if}(-t)$.

Going to second order perturbation theory in the anisotropic interaction, we find

$$[q_{if}(t) - 1] = K_i(t) + K_f(t), \qquad (12)$$

with

$$K_f(t) = -\frac{1}{\hbar^2} \sum_{J\vec{k}} \rho(\varepsilon_J)\ \rho(\varepsilon_{\vec{k}})$$

$$\cdot \sum_{j_f' J' \vec{k}'} |\langle j_f J \psi_{\vec{k}} | V | j_f' J' \psi_{\vec{k}'} \rangle|^2\ f(t), \qquad (13)$$

where $\rho(\varepsilon_J)$, $\rho(\varepsilon_{\vec{k}})$ are density matrices for the internal states of the perturbers, and the translational motion of the relative coordinate (respectively), and with

$$f(t) = -\frac{i}{\omega_{\alpha\beta}} \{t - \frac{i\ (e^{-i\omega_{\alpha\beta}t} - 1)}{\omega_{\alpha\beta}}\}, \qquad (14a)$$

$$= \frac{[1-\cos(\omega_{\alpha\beta}t)]}{\omega_{\alpha\beta}^2} - \frac{i}{\omega_{\alpha\beta}^2} [\omega_{\alpha\beta}t - \sin(\omega_{\alpha\beta}t)] \qquad (14b)$$

with

$$\omega_{\alpha\beta} \equiv \frac{1}{\hbar} (\varepsilon_{j_f J \vec{k}} - \varepsilon_{j_f' J' \vec{k}'}). \qquad (15)$$

Similarly

$$K_i(t) = -\frac{1}{\hbar^2} \sum_{J\vec{k}} \rho(\varepsilon_J)\, \rho(\varepsilon_{\vec{k}}) \cdot \sum_{j_i' J' \vec{k}'} |\langle j_i J \psi_{\vec{k}} | V | j_i' J' \psi_{\vec{k}'} \rangle|^2 \, \tilde{f}(t), \tag{16}$$

$$\tilde{f}(t) = \frac{i}{\omega_{\alpha\beta}} \{(t - i\beta\hbar) + \frac{i}{\omega_{\alpha\beta}} (e^{i\omega_{\alpha\beta}(t-i\beta\hbar)} - 1)\}, \tag{17a}$$

or

$$\tilde{f}(t) = \frac{1}{\omega_{\alpha\beta}^2} [1 + \beta\hbar\omega_{\alpha\beta} - e^{\beta\hbar\omega_{\alpha\beta}} \cos \omega_{\alpha\beta} t] + \frac{i}{\omega_{\alpha\beta}} [\omega_{\alpha\beta} t - e^{\beta\hbar\omega_{\alpha\beta}} \sin \omega_{\alpha\beta} t] \tag{17b}$$

$$\omega_{\alpha\beta} \equiv \frac{1}{\hbar} (\varepsilon_{j_i J \vec{k}} - \varepsilon_{j_i' J' \vec{k}'}). \tag{18}$$

For simplicity, in writing down the above expressions we have suppressed Clebsch-Gordon coefficients and m-summations, which are important only for numerical calculations.

For large times, it may be shown that the above equations yield the impact approximation[4,5] (including both width and shift), i.e. the argument of the exponential in Eq. (10) is a linear function of t.

At very small t, the correlation function behaves essentially as a Gaussian. This implies that all time-derivatives of $C_{if}(t)$ exist at t = 0. This in turn implies that all moments[2] of the lineshape function (in the frequency domain) are well-defined and finite.

In order to implement the above theory for numerical computation, the following tasks need to be performed:

a. The Clebsch-Gordon algebra must be done (this has already been carried out for the case where the anisotropic interaction V is taken to be a dipole-dipole interaction.

b. The relative coordinate wave functions $|\psi_{\vec{k}}>$, which satisfy

$$[\frac{\hbar^2\nabla^2}{2m} + V_0(r)]|\psi_{\vec{k}}> = \varepsilon_{\vec{k}}|\psi_{\vec{k}}>, \tag{19}$$

where V_0 is the isotropic potential, need to be calculated.

c. Matrix element of the form

$$<\psi_{\vec{k}'}|\frac{1}{r^3}|\psi_{\vec{k}}>$$

must be evaluated.

d. Various summations over quantum indices need to be carried out, and a Fourier transform of $C_{if}(t)$ must be performed to yield the lineshape function $C_{if}(\omega)$.

In previous reports we have discussed some of the problems associated with obtaining an accurate Fourier transform of $C_{if}(t)$. In particular, one must accurately sum contributions of $C_{if}(t)$ from time values which may differ by three orders of magnitude (e.g. the difference between a duration of collision τ_d, and a time between collisions τ_c). We have also discussed a "difference function" technique for performing the Fourier inversion. In this method, one writes

$$C(t) = C_{Basis}(t) + C_{diff}(t), \tag{20a}$$

where

$$C_{diff}(t) = C(t) - C_{Basis}(t). \tag{20b}$$

The basis function is chosen to have two basic properties:

a. $C_{Basis}(t)$ has an analytic Fourier transform.

b. $C_{diff}(t)$ vanishes at large t, eliminating the need to integrate over large t values.

We have previously reported application of this scheme to simple (real) correlation functions such as the Anderson-Weiss correlation function. Here we briefly present some results for a complex-valued correlation function, with a time-dependent f(t) function given by Eq. (14).

The function we have chosen has the form

$$C(t) = e^{-\alpha F(t)}, \tag{21}$$

where α is a constant, and

$$F(t) = \int_0^\infty \sqrt{\omega_k}\, d\omega_k\, e^{-\frac{\hbar\omega_k}{k_B T}} f(t), \tag{22}$$

with

$$f(t) = \frac{1-\cos(\omega_k-\omega_{rot})t}{(\omega_k-\omega_{rot})^2} + i\,\frac{1}{(\omega_k-\omega_{rot})}\left\{t - \frac{\sin(\omega_k-\omega_{rot})t}{\omega_k-\omega_{rot}}\right\}. \tag{23}$$

Although this model represents a rather gross simplification of the general theory, we note that f(t) has the same time-dependence as in Eq. (14), with the identification $\omega_{\alpha\beta} \to (\omega_{rot} - \omega_k)$. If we choose α to have the value

$$\alpha = \frac{\Gamma}{\pi\sqrt{\omega_{rot}}}\, e^{\hbar\omega_{rot}/k_B T}, \tag{24}$$

then Γ can be interpreted as the impact-approximation half-width, and the long-time behavior of C(t) is given approximately by

$$C(t) = e^{-\Gamma|t|}$$

$$\cdot \exp\{- i\Gamma t [e^{\frac{\hbar\omega_{rot}}{k_BT}} (\frac{k_BT}{\hbar\omega_{rot}})^{1/2} - 2 \int_0^{\frac{\hbar\omega_{rot}}{k_BT}} dy\, e^{y^2}]\}. \quad (25)$$

(The above expression ignores small terms in the arguments of the exponentials which behave as constants at large t.)

To apply the difference function method, we have modeled the basis function $C_{Basis}(t)$ such that the real part is a convolution (in time) of a Gaussian and an exponential, and the imaginary part is the derivative of such a function. This choice has the correct properties that Re C(t) is even, while Im C(t) is odd. The adjustable constants in the convolutions are chosen such that $C_{diff}(t) \to 0$ for large t. We have also been able to choose $C_{basis}(t)$ such that $C_{diff}(t)$ also vanishes at t = 0.

It turns out that one can obtain an analytic approximation to the Fourier transform of Eq. (21), which is valid in the far wing, by expanding to first order in the density, i.e.

$$C(t) \simeq 1 - \alpha F(t). \quad (26)$$

This can be Fourier-transformed analytically, and discarding spurious delta function contributions at the line center $\omega = 0$ (which are improperly treated by the above expansion), one obtains the result

$$R(\omega) \equiv \frac{C(\omega)}{C_{Lor}(\omega)}$$

$$= e^{-\frac{\hbar\omega}{k_BT}} (\frac{\omega_{rot}+\omega}{\omega_{rot}})^{1/2} \theta(\omega_{rot}+\omega), \quad (27)$$

where θ is the unit step function

$$\theta(x) = 1, \; x \geq 0$$

$$= 0, \; x < 0,$$

and where

$$C_{Lor}(\omega) = \frac{1}{\pi} \frac{\Gamma}{\omega^2+\Gamma^2}$$

is the Lorentzian lineshape function.

In Figures 1 and 2 we show plots of the real and imaginary parts of the difference function $C_{diff}(t)$, as used in the numerical Fourier transform of C(t). These functions are plotted versus a length variable $x = 2\pi ct$, and the main point to notice is that the difference functions oscillate to zero at large x (large t).

The results of our numerical Fourier transform, with the choice of parameters $\omega_{rot} = 100\ cm^{-1}$, $T = 296°K$ are shown in Figure 3. To within plotting accuracy, the results agree well with the predictions of the analytic formula (27).

The above model is rather too crude to assign much physical significance, e.g. in a more realistic model, ω_{rot} would be replaced by a whole distribution of frequencies (both positive and negative) determined by the collision dynamics and multipole selection rules. In spite of these complications, the results of the model calculation provide some confidence that an accurate Fourier transform of realistic correlation functions can be obtained using the "difference function" technique.

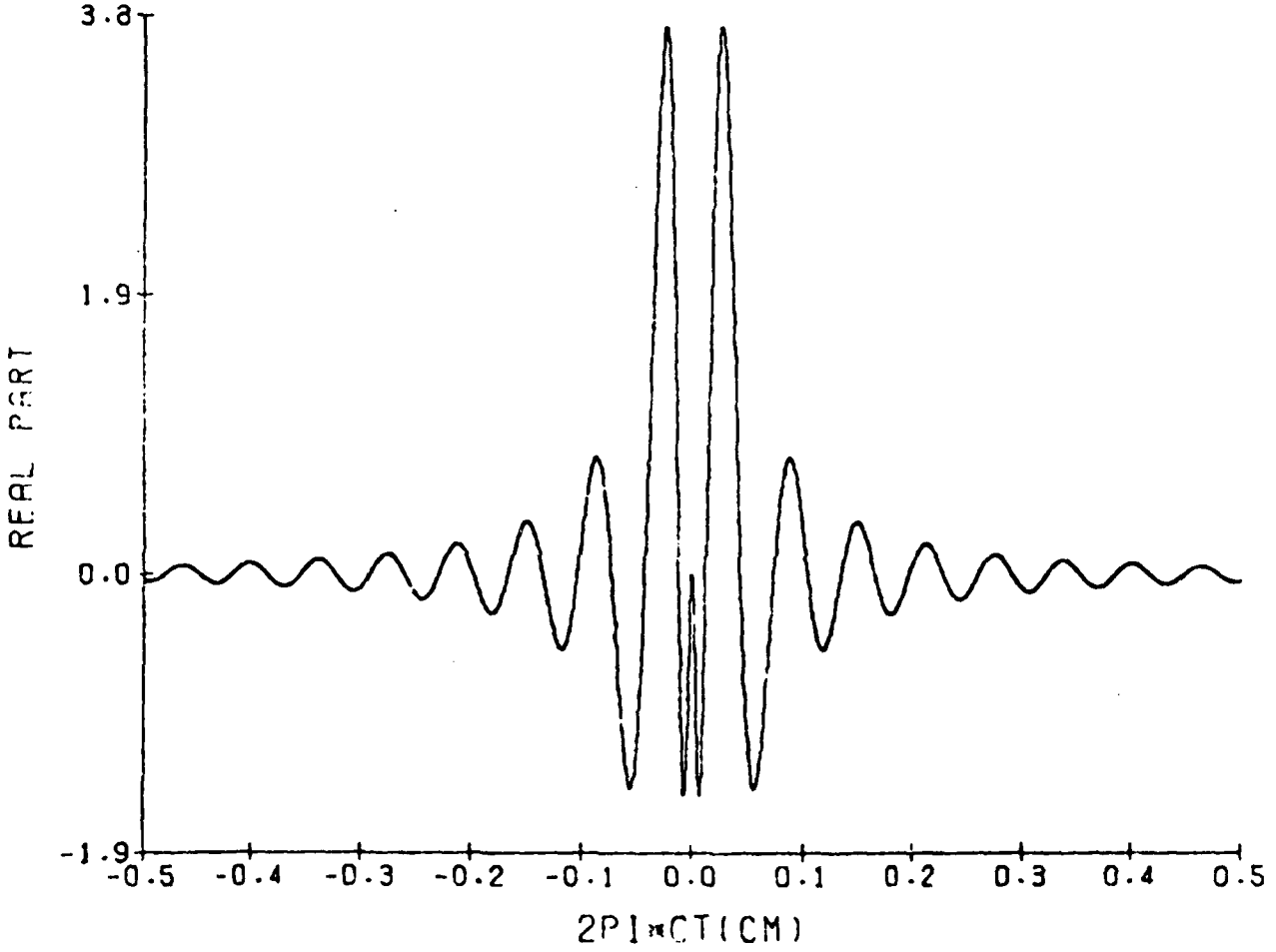

Figure 1. Real part of the difference function $C_{diff}(t)$ plotted vs. the length variable $x = 2\pi ct$.

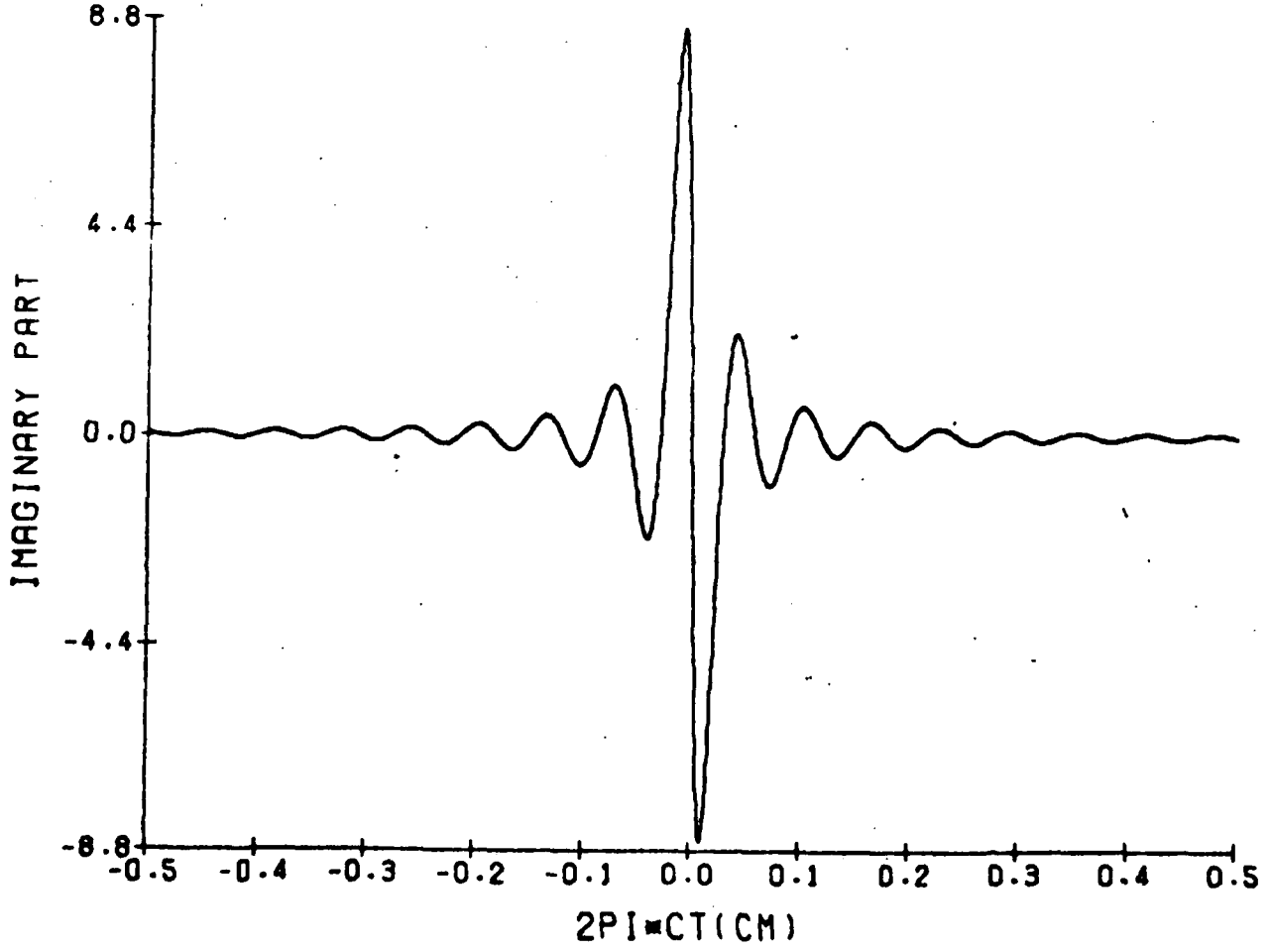

Figure 2. Imaginary part of the difference function $C_{diff}(t)$.

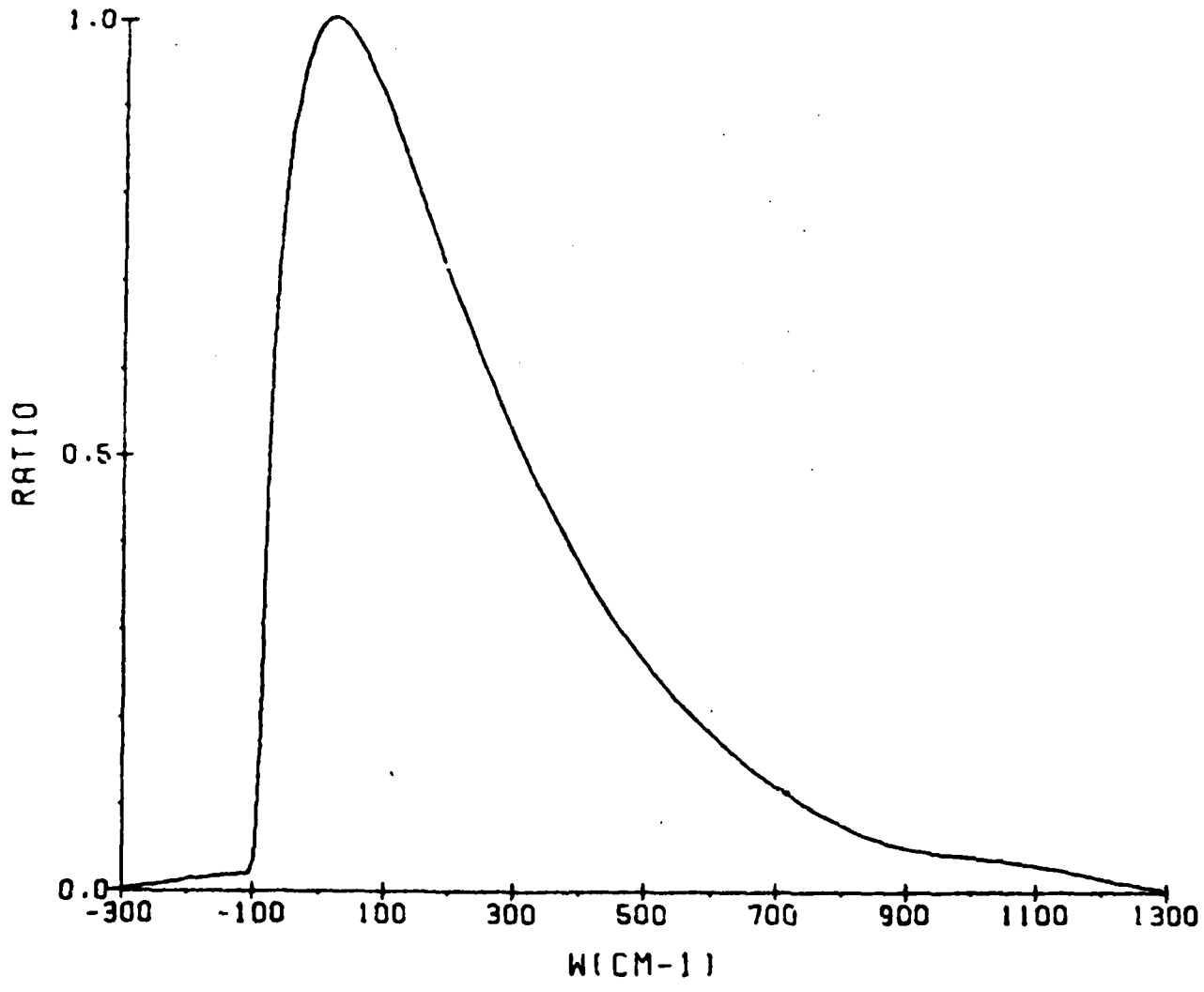

Figure 3. The ratio of the lineshape function $C(\omega)$ to the Lorentzian lineshape function for the case $\omega_{rot} = 100\ cm^{-1}$, $T = 296°K$.

3.0 SOFTWARE FOR UPDATING ASYMMETRIC ROTORS ON THE AFGL LINE PARAMETERS ATLAS

The procedure we have employed to update H_2O bands for the AFGL Line Parameters Compilation is based on the procedure which we first developed to treat the ν_2 band of $H_2O(161)$. The development of the method is based on two demands; to eliminate entirely the making of typographical errors when updating bands and, given an old and a new data set, to construct from these data the best and most complete data set possible for addition to the AFGL line atlas. Some of the problems that can occur when dealing with very large data bases are: 1) usually the new data does not fully replace the old, thus the final data set must be a controlled merging of the two sets; 2) when parts of the new data set are in question, both new and old data are carefully analyzed to determine which is the better and hence which will be retained for the next version of the atlas; 3) sometimes multiple quantum assignments of the lines occur, when they do they must be found and eliminated. Once the procedure has been applied to a band, we generate comparisons of the old data to the new data to display the changes that have occurred. We have also found it advantageous to keep track of the source of each parameter for both future updating and for discussions with the users of the AFGL line atlas.

Below we give a general discussion of the software systems that make up the procedure, and in Figure 4 we give a flow chart of the method. Although there are some changes that must be made from band to band and from molecule to molecule, we have attempted to keep the procedure as general as possible for asymmetric rotor molecules (i.e. H_2O, O_3, SO_2; etc.). To date the procedure has only been applied to vibration-rotation bands of the water molecule, and in Table 1 we list the updated bands along with pertinent information describing the data sets. All the new parameters, i.e. line

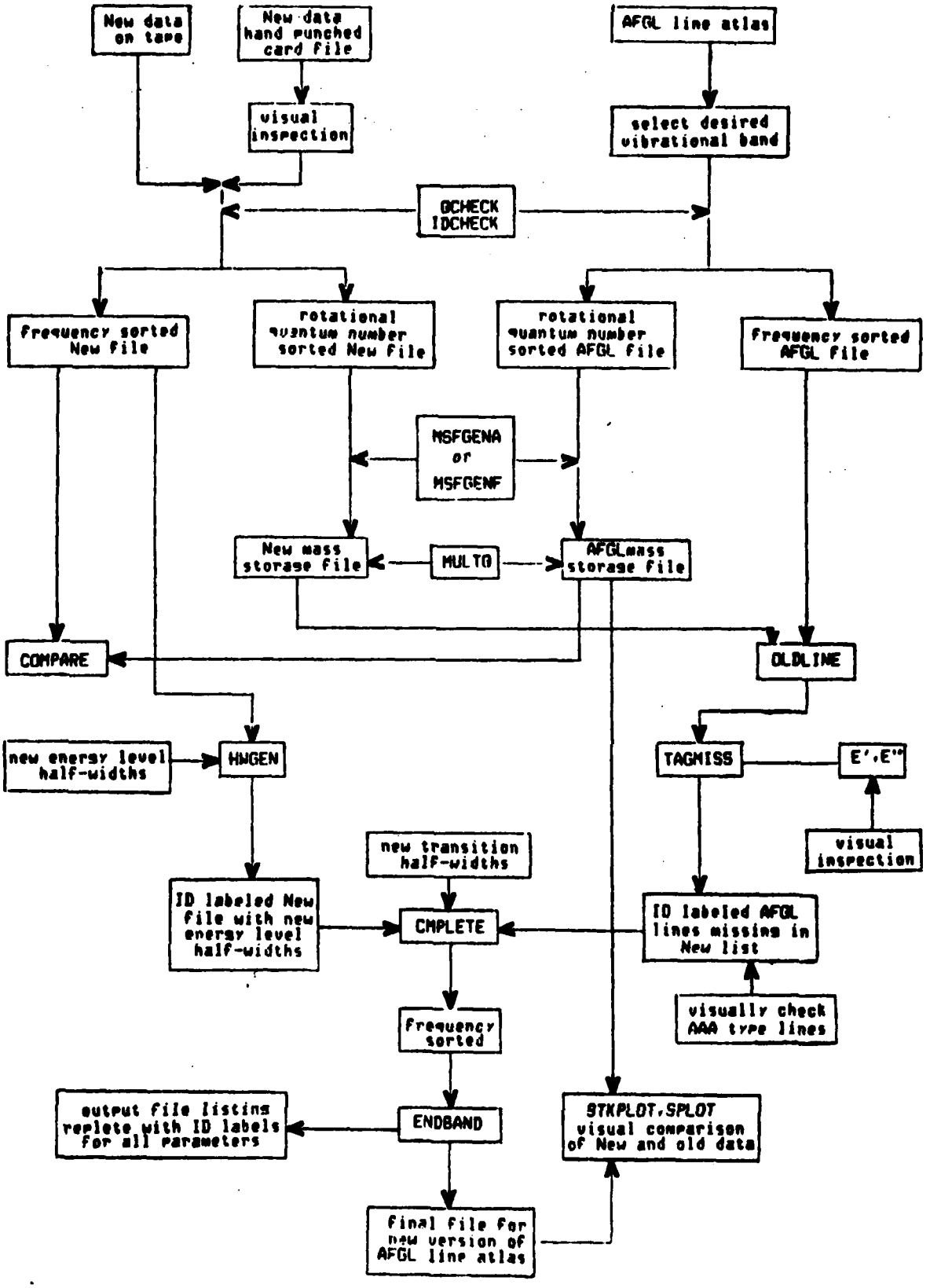

Figure 4. Flow chart of update procedure.

Table 1. Updated Bands of Water

Band		Isotope	# Lines	ν^{a}_{Low} cm^{-1}	ν^{b}_{High} cm^{-1}	S^{c}_{Min}	S^{d}_{Max}	Band Sum[e]
010	010	161	750	0.401	1029.459	0.0102	0.1120	2.225
020	010	161	930	877.309	2439.139	1.010	0.0234	0.8152
010	000	161	1807	640.503	2821.064	3.170	29.00	1038.0
100	010	161	628	1221.409	2615.794	1.000	0.0006	0.0192
001	010	161	563	1298.118	2767.460	1.010	0.0010	0.0263
020	000	161	1146	2039.167	4402.334	3.030	0.3580	7.537
100	000	161	1381	2851.380	4604.072	3.010	2.020	48.62
001	000	161	1750	2821.544	4517.305	3.020	22.20	692.5
030	000	161	662	4250.753	5931.119	2.910	0.0042	0.0396
110	000	181	443	4791.701	5727.490	1.000	0.0007	0.0056
110	000	161	991	4602.671	6005.294	3.230	0.3600	3.716
011	000	181	734	4808.087	5962.892	1.000	0.0049	0.1476
011	000	161	1306	4609.391	6254.372	3.100	2.760	80.42
040	000	161	215	5904.037	7189.667	10.00	0.0001	0.0018

a. Minimum Frequency of Band.

b. Maximum Frequency of Band.

c. Minimum Line Strength of Band (10^{-27} cm^{-1}/molecule cm^{-2}).

d. Maximum Line Strength of Band (10^{-20} cm^{-1}/molecule cm^{-2}).

e. Sum of Line Strengths of Band Given in 10^{-20} cm^{-1}/molecule·cm^{-2}.

positions, intensities, and lower state energies of transitions for these bands are taken from C. Camy-Peyret, J. M. Flaud, et al,[6-17] and we wish to thank these authors for making their data available to us. All of these bands are present on the 1980 version of the AFGL Line Parameters Compilation.

The start of the procedure is dependent on the form in which the new data is available to us. If we are not able to obtain the data directly from the source, we construct hand punched card files of the published data. These files must be carefully checked for typographical errors. Once the new file is verified to match the published results we extract the corresponding band from the AFGL tape and both files (new and old) are run through the programs QCHECK and IDCHECK which test quantum assignments according to selection rules and band assignments, respectively. From this point on we simply refer to the data used in updating the band as the "new data" and the data from the AFGL tape as "old data."

Once we are assured the data files are correct we frequency-sort each file and rotational-quantum-number-sort (J', Ka', Kc', J", Ka", Kc") each file. The new quantum-number-sorted file is input to the program MSFGENF, and the old quantum-number-sorted file is input to the program MSFGENA. MSFGENF and MSFGENA create mass storage files of the new and old data sets respectively. These mass storage files are constructed by the unique rotational quantum number assignment of each transition and can reduce the effort of searching for a particular line by several orders of magnitude. The resulting mass storage file has as its key the upper state rotational quantum numbers, and each record contains all transitions with the same upper state assignments and different lower state assignments. The index key of each record is calculated by the formula INDX = J'(J'+1) + Ka' - Kc' + 1. If a file does not contain any transitions belonging to a

particular index, a flag is written to that index meaning no information available for that index. This check is incorporated into all programs which read the mass storage files.

Once the mass storage files (MSF's) are constructed they are tested by the program MULTQ which checks for multiple assignments which, due to the structure of the MSF's, are easily uncovered. If any multiple assignments are found, the extra lines are deleted from the quantum-number-sorted file, the MSF is reconstructed and checked again by MULTQ, and this is repeated until the final MSF's are known to be correct.

We next work with the new and old frequency sorted files and the new and old mass storage files. As stated earlier, it is required to have a tabulated listing of the differences between the new and old data. This is done by the program COMPARE which uses the frequency-sorted new file and the old mass storage file. This yields a line-by-line listing of the difference in the data sets along with several types of flags that signal large differences in the data. These listings have proved very useful in consultations with users of the AFGL Compilation.

The frequency-sorted new file is also used in the program HWGEN. The new files for H_2O usually contain the transition frequency, the strength of the transition, the lower state energy, and quantum identification of the transition. Before the file can be used for the Atlas we need to add the air-broadened half-widths for the transitions. HWGEN adds to the new file the corresponding half-widths as calculated by Davies and Oli.[18] In addition, the program also adds ID labels to identify the source of each datum (five ID labels in all - source of the transition quantum numbers, the source of the frequency, the strength, the half-width, and the lower state energy). The ID becomes important in future references concerning the quality of the data for a particular line. The ID labeled file containing the corrected half-widths is now referred to as the frequency-sorted new file.

The frequency-sorted old file and the new MSF are used in the program OLDLINE which selects all lines in the old data which are not present in the new data. This file, which is called the missing line file, is then run in the program TAGMISS. The TAGMISS program uses two MSF's containing the rotational energy levels of the upper and lower vibrational states of the band in question to add to the missing-line file the line positions and lower state energies derived from the new data. This is not always possible since some of the energy levels for certain vibrational states are unknown; in these cases the old data is retained. The program adds ID labels to the lines according to the types of changes that have occurred. Finally all lines that retain the old frequency are inspected and the line position is estimated from the new data. This is done to remove any obvious typographical errors in the old data.

At this stage of the procedure we have an ID labeled new file and an ID labeled missing line file from the old data. These two files are fed into CMPLETE which, using mass storage techniques, adds to the two files whenever possible more accurate half-widths computed by a method similar to reference 18 but with a more correctly determined Anderson parameter b_0 for the complete transition i → f. In carrying this out, gram corrects the ID labels when necessary and merges the two files. The file is frequency sorted and used in the program ENDBAND which writes the final file to output (replete with ID labels for all parameters), and writes a final file to AFGL format for addition to the next edition of the AFGL Line Parameter Atlas. ENDBAND also gives useful statistics on the data making up the band.

The final file is used with the old MSF to generate a series of plots that visually display the changes that resulted from the updating procedure. This presently includes a plot of the changes in the line positions and several plots of the changes in the line intensities. Examples of the plots are given in Figures 5 to 9.

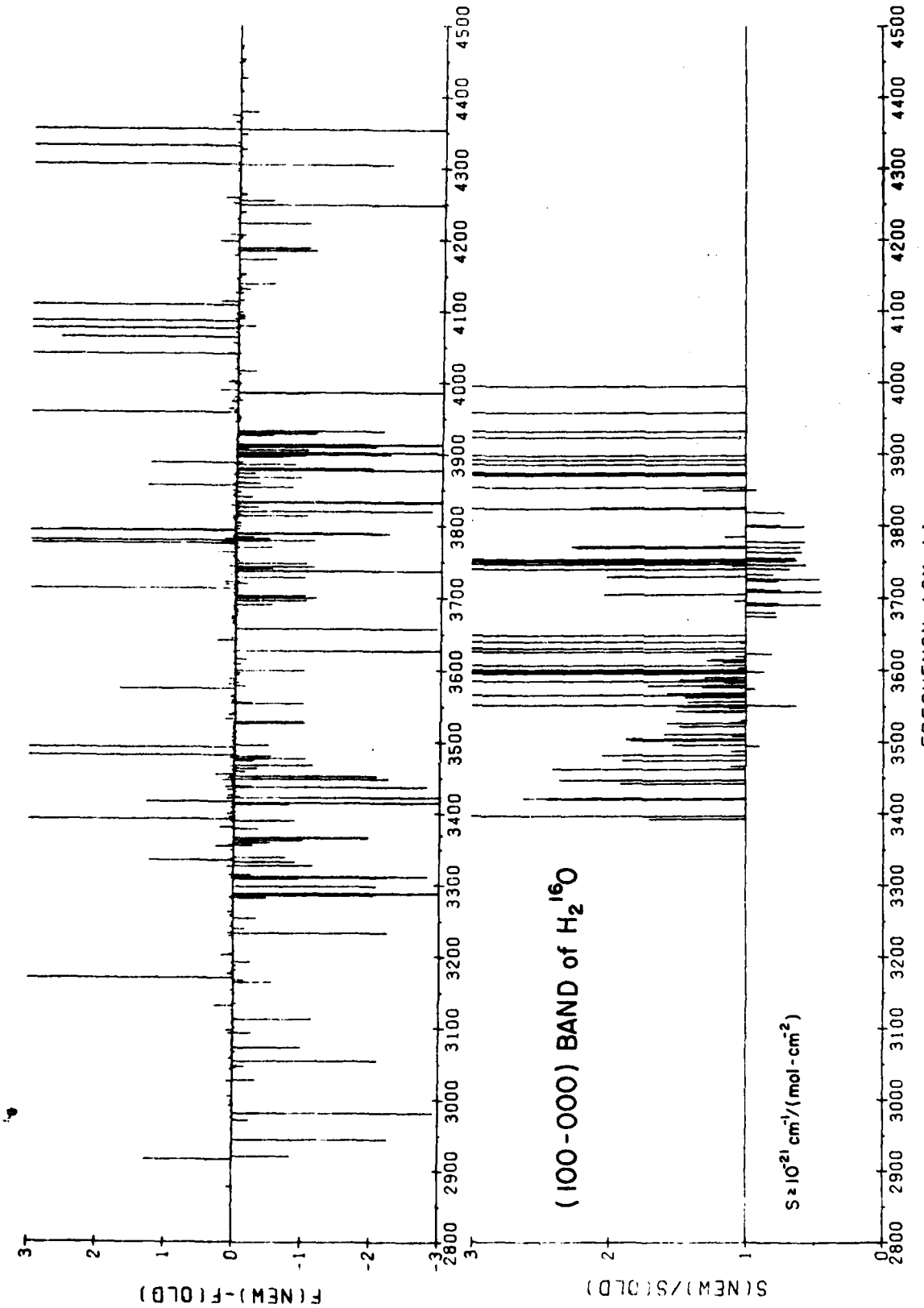

Figure 5. Comparison of 1980 ν_1 file to 1978 ν_1 file.

a. Frequency

b. Strong intensities

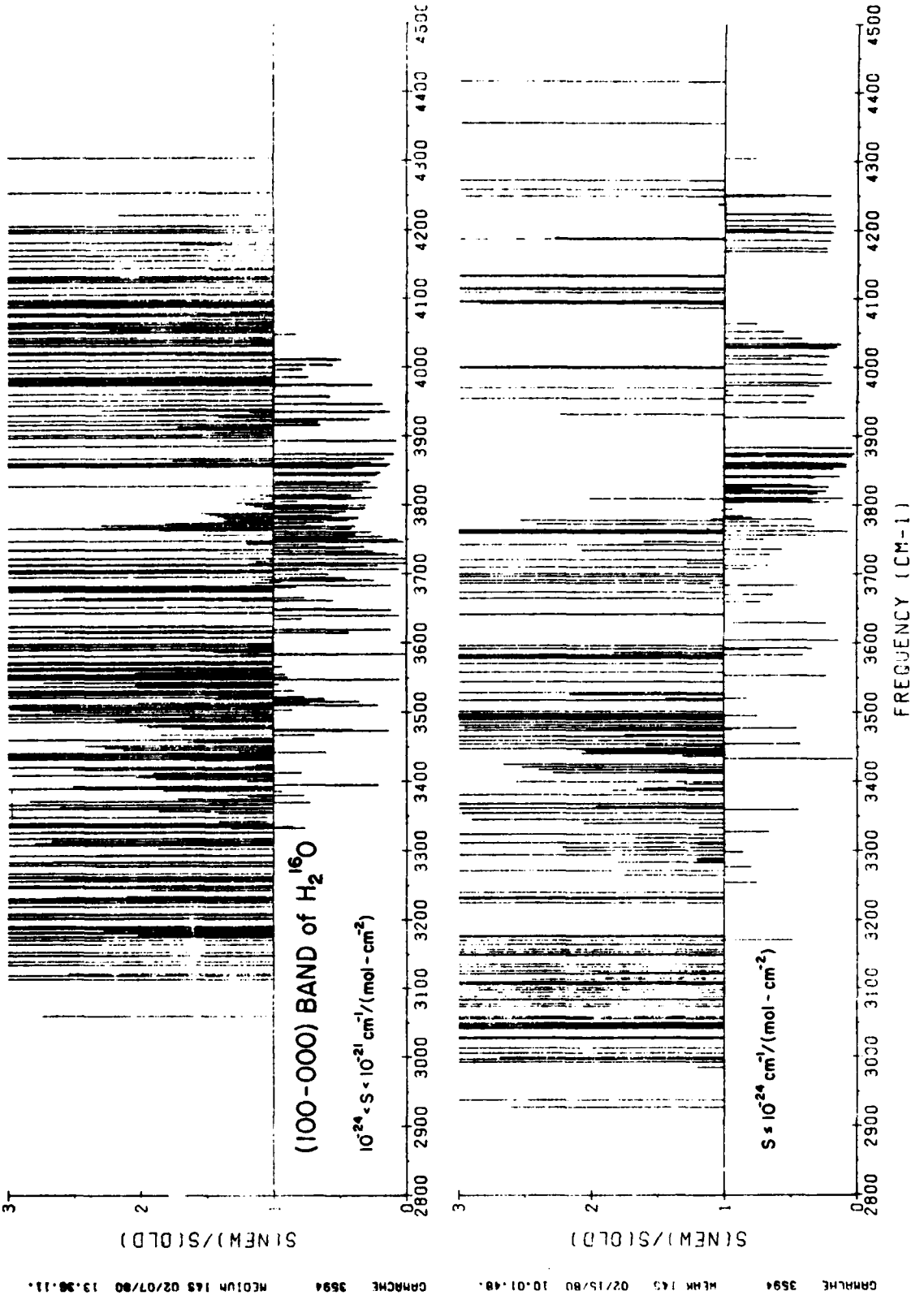

Figure 6. Comparison of 1980 ν_1 file to 1978 ν_1 file

a. Intermediate intensities

b. Weak intensities

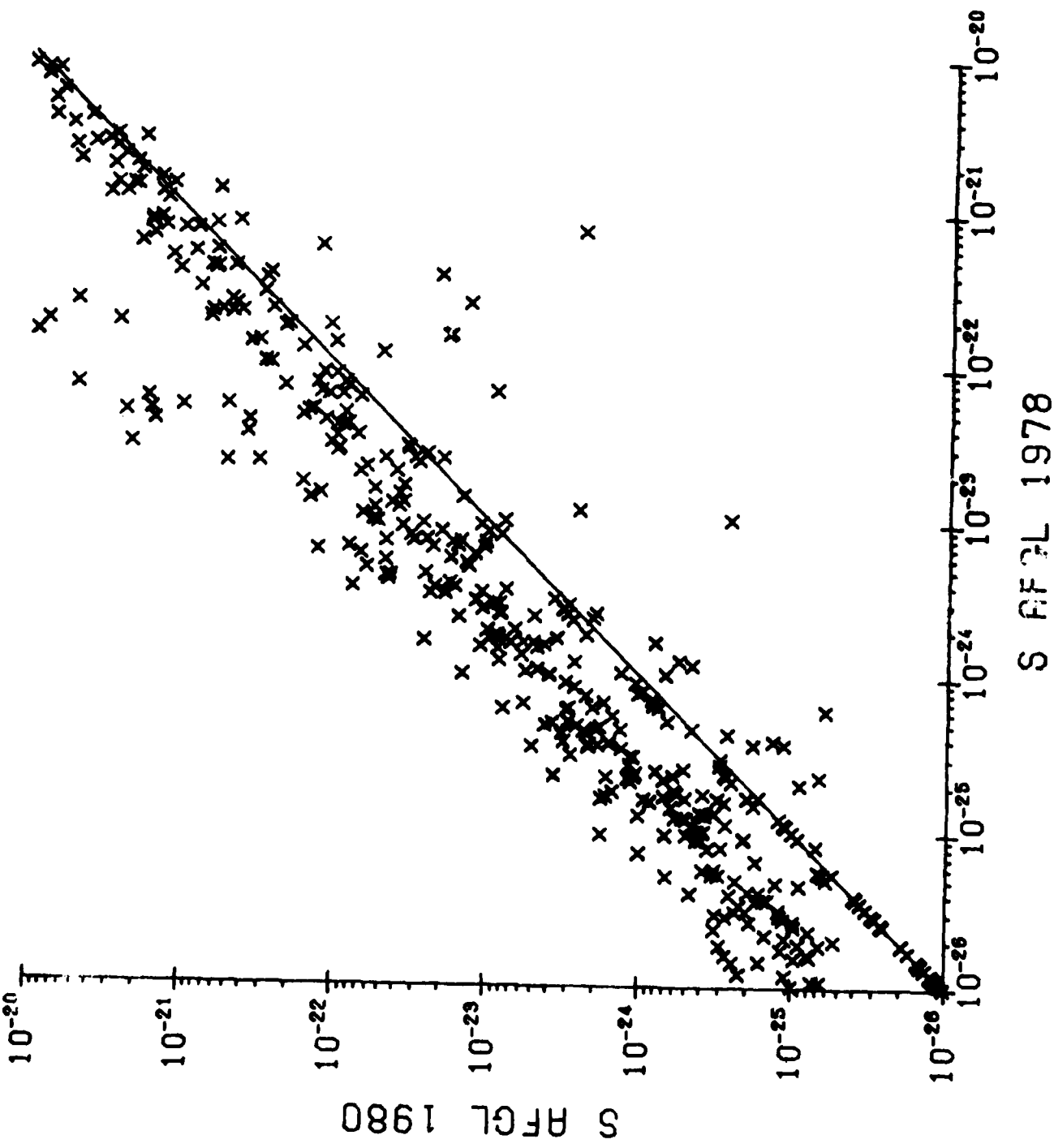

Figure 7. Comparison of strengths from 1980 ν_1 file to 1978 ν_1 file, P-Branch.

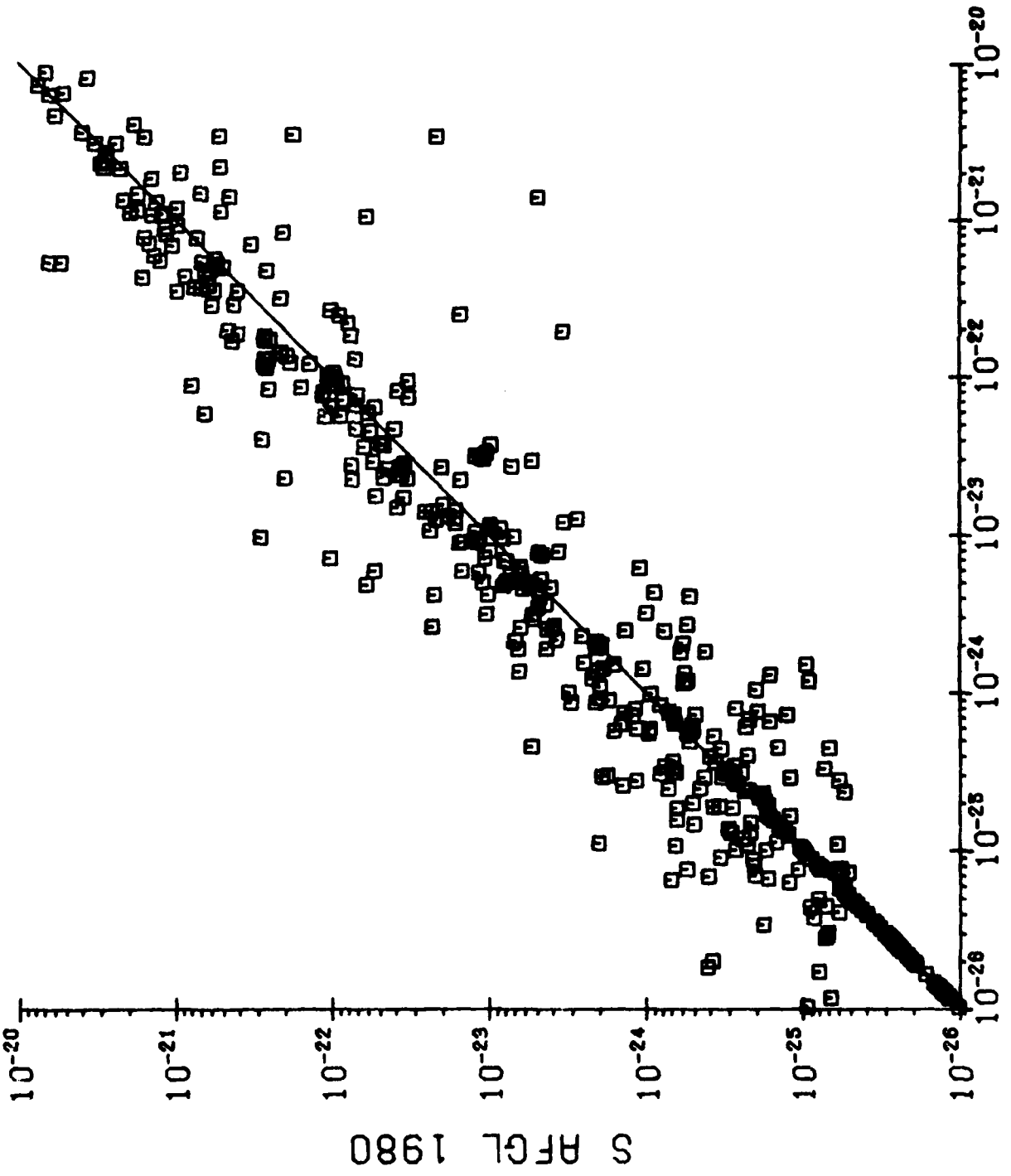

Figure 8. Comparison of strengths from 1980 ν_1 file to 1978 ν_1 file, Q-Branch.

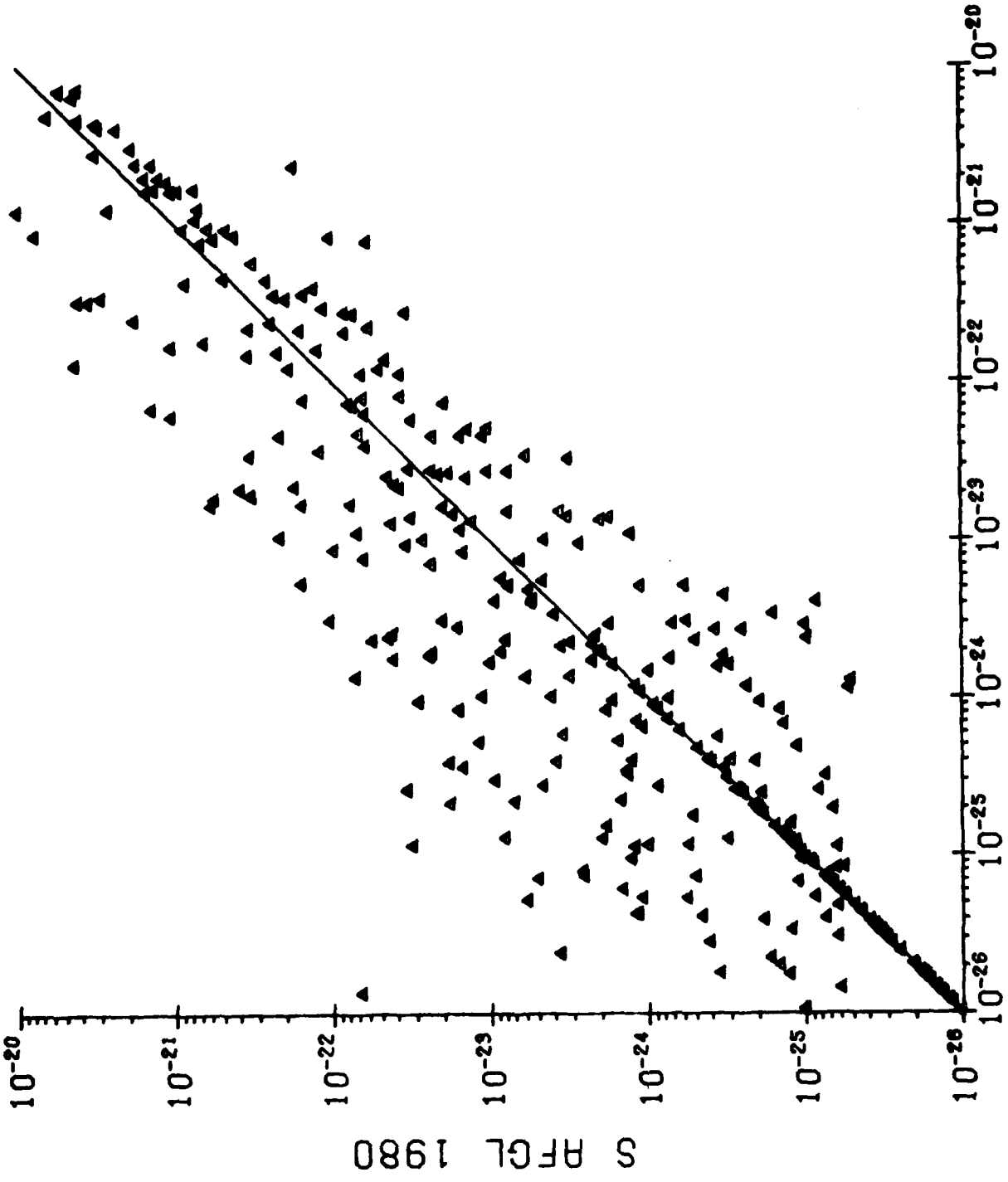

Figure 9. Comparison of strengths from 1980 ν_1 file to 1978 ν_1 file, R-Branch.

The procedure discussed above has been successfully applied to the 14 bands of H_2O listed in Table 1.

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A P P E N D I X A

The Dipole Autocorrelation Function for Molecular Pressure Broadening: A Quantum Theory Which Satisfies the Fluctuation-Dissipation Theorem.

THE DIPOLE AUTOCORRELATION FUNCTION FOR MOLECULAR PRESSURE BROADENING: A QUANTUM THEORY WHICH SATISFIES THE FLUCTUATION-DISSIPATION THEOREM†

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ABSTRACT

The dipole correlation function for molecular pressure broadening is treated in a quantum theory which rigorously satisfies the Fluctuation Dissipation Theorem on a microscopic level. The two basic approximations in the theory are the uncoupled-line and binary collision approximations. In the present paper, the consequences of the formulation are analyzed up to second order in the anisotropic molecular interaction. An isotropic potential is also included, which, in principle, is treated exactly. At large times it is shown that the theory reduces to the well-known impact approximation. At short times, an autocorrelation function of Gaussian form, with a renormalization of the initial state occupancy is obtained. It is found that the qualitative features discussed above are unaltered in higher order perturbation theory. The results imply that all time-derivatives of the autocorrelation function at $t = 0$ exist. This further implies that all moments of the lineshape function in the frequency domain exist, hence that the lineshape function must decay "exponentially" sufficiently far in the wings.

I. INTRODUCTION

In the calculation of molecular pressure broadening, extensive use has been made of the autocorrelation function[1-3] for the dipole moment operator in the time domain. Using this method, the power spectrum for absorbed or emitted radiation is obtained from the Fourier transform of the autocorrelation function. This result follows from the quantum analog of the Wiener-Khintchine theorem[1] for classical correlation functions. In spite of the diverse formulations[4-12] which may be found in the literature, it appears that certain aspects of the theory remain incomplete or have not been adequately discussed.

It is generally assumed that the far wings of spectral transitions are strongly influenced by the small time behavior of the autocorrelation function. However, any rigorous treatment for small times must certainly satisfy the Fluctuation-Dissipation Theorem (FDT).[1,13-16] The FDT has been incorporated into a number of essentially phenomenological theories,[17-19] using the Egelstaff[20,21]-Schofield complex-time transformation. These theories force the FDT to be valid on a line-by-line basis, using an autocorrelation function involving a number of adjustable parameters, typically a time between collisions, τ_c, and something analogous to the duration of collision, τ_d. To our knowledge, no <u>microscopic</u> formulation which satisfies the FDT has been presented in the literature. In this paper we provide such a formulation. The present theory will also

provide an explicit microscopic description for the short-time behavior of the autocorrelation function, and for the transition to the long-time regime where the impact approximation is generally considered to be valid. These two aspects have remained unclear in most previous formulations.

In the present paper we shall make essentially two approximations; (a) the binary collision approximation, and (b) we shall eventually ignore line-coupling effects.[5,6] For problems involving atmospheric densities, the binary collision approximation appears to be justified from experimental observations. The neglect of line-coupling effects is more serious, however, construction of a general theory which includes such effects rigorously, and which also satisfies the FDT, appears to be a more complicated problem. Within the two approximations above, we shall show, at small times, that the autocorrelation function for each line is of Gaussian form. This implies that all time-derivatives exist at $t = 0$, hence that all moments[17] of the lineshape function must also exist. The transition to the long-time impact regime will also be examined.

II. GENERAL THEORY

We shall write the absorption coefficient (cm^{-1}) in the form[17]

$$\alpha(\omega) = \frac{4\pi^2\omega\, n_{rad}}{3c}\,\chi''(\omega) \qquad \text{(II-1)}$$

$$\chi''(\omega) = \tanh\left(\frac{\beta\hbar\omega}{2}\right)\int_{-\infty}^{\infty}\frac{dt}{2\pi\hbar}\,e^{-i\omega t}\,[\phi(t)+\phi(-t)] \qquad \text{(II-2a)}$$

$$= (1-e^{-\beta\hbar\omega})\int_{-\infty}^{\infty}\frac{dt}{2\pi\hbar}\,e^{-i\omega t}\,\phi(t) \quad , \qquad \text{(II-2b)}$$

$$= \int_{-\infty}^{\infty}\frac{dt}{2\pi\hbar}\,e^{-i\omega t}\,[\phi(t)-\phi(-t)] \quad . \qquad \text{(II-2c)}$$

In these equations, n_{rad} is the number density of radiating molecules, $\beta = (k_B T)^{-1}$, and $\phi(t)$ is the autocorrelation function given by

$$\phi(t) = Tr\,\{\rho(H)\vec{\mu}(0)\cdot\vec{\mu}(t)\} \quad , \qquad \text{(II-3a)}$$

$$\phi(-t) = Tr\,\{\rho(H)\vec{\mu}(0)\cdot\vec{\mu}(-t)\} \quad , \qquad \text{(II-3b)}$$

$$= Tr\,\{\rho(H)\vec{\mu}(t)\cdot\vec{\mu}(0)\} \quad , \qquad \text{(II-3c)}$$

where $\vec{\mu}(t)$ is the Heisenberg operator

$$\vec{\mu}(t) = e^{\frac{iHt}{\hbar}}\,\vec{\mu}(0)\,e^{-\frac{iHt}{\hbar}} \quad , \qquad \text{(II-4)}$$

and

$$\rho(H) = e^{-\beta H}/Tr\,\{e^{-\beta H}\} \qquad \text{(II-5a)}$$

$$= e^{-\beta H}/Z \quad , \qquad \text{(II-5b)}$$

is the canonical density matrix.

The Hamiltonian H is for a system consisting of one radiating (absorbing) molecule, and N_p perturbers with which it may interact.

The equivalence of formulas (II-2a) - (II-2c) is contained in the time domain statement[17] of the FDT, i.e.

$$\phi(-t) = \phi(t + i\beta\hbar) \quad . \quad \text{(II-6)}$$

This result is readily proven from Eqs. (II-3a - II-3c) using cyclic invariance and the fact that $e^{\pm iHt/\hbar}$ commute with $\rho(H)$; Eq. (II-6) must also be consistent with the relation

$$\phi(-t) = \phi(t)^* \quad , \quad \text{(II-7)}$$

which guarantees that $\alpha(\omega)$ is real.

From Eqs. (II-3a - II-3c) we may write

$$\phi(t) = Z^{-1} \cdot Tr\{\vec{\mu}\, e^{\frac{iHt}{\hbar}} \cdot \vec{\mu}\, e^{-\frac{iH}{\hbar}(t-i\beta\hbar)}\} \quad \text{(II-8a)}$$

$$\phi(-t) = \phi(t + i\beta\hbar)$$

$$= Z^{-1} \cdot Tr\{e^{\frac{iH}{\hbar}(t+i\beta\hbar)}\, \vec{\mu} \cdot e^{-\frac{iHt}{\hbar}}\, \vec{\mu}\} \quad . \quad \text{(II-8b)}$$

In what follows it will be convenient to decompose the Hamiltonian H as follows:

$$H = H_0 + V \quad , \quad \text{(II-9)}$$

where H_0 contains the unperturbed energies of the molecules and any purely <u>isotropic</u> interactions, V_0, which do not involve the internal states, i.e. V_0 depends only on center of mass separations. The perturbation V is then taken to contain the <u>anisotropic</u> interactions between the radiator and the perturbing molecules.

Now in Eqs. (II-8a - II-8b) we introduce the time-development operator defined by

$$e^{-\frac{iHt}{\hbar}} = e^{-\frac{iH_0 t}{\hbar}} U(t) \qquad ,(II\text{-}10a)$$

$$e^{\frac{iHt}{\hbar}} = U(t)^{\dagger} e^{\frac{iH_0 t}{\hbar}} \qquad ,(II\text{-}10b)$$

or, more generally, for complex t

$$e^{-\frac{iHz}{\hbar}} = e^{-\frac{iH_0 z}{\hbar}} U(z) \qquad ,(II\text{-}11a)$$

with adjoint relation

$$e^{\frac{iHz^*}{\hbar}} = U(z)^{\dagger} e^{\frac{iH_0 z^*}{\hbar}} \qquad .(II\text{-}11b)$$

From the above relations, one readily sees that U(t) is unitary for real t. Making use of these definitions, we obtain

$$\phi(t) = \nu \, Tr\{\rho(H_0)U(t-i\beta\hbar)\vec{\mu} \, U(t)^{\dagger} \cdot e^{\frac{iH_0 t}{\hbar}} \vec{\mu} \, e^{-\frac{iH_0 t}{\hbar}}\} \qquad ,(II\text{-}12a)$$

and

$$\phi(-t) = \phi(t + i\beta\hbar)$$

$$= \nu \, Tr\{\rho(H_0) \, e^{\frac{iH_0 t}{\hbar}} \vec{\mu} \, e^{-\frac{iH_0 t}{\hbar}} \, U(t) \cdot \vec{\mu} \, U(t-i\beta\hbar)^{\dagger}\} \qquad ,(II\text{-}12b)$$

where $\rho(H_0) = e^{-\beta H_0}/Tr\{e^{-\beta H_0}\}$, is the unperturbed density matrix, and where ν is the ratio

$$\nu \equiv \frac{Z_0}{Z} = \frac{Tr\{e^{-\beta H_0}\}}{Tr\{e^{-\beta H}\}} \qquad . (II\text{-}13)$$

From Eq. (II-12b) it is clear, in a trivial fashion, that the FDT is still satisfied at this point. However, there are ways of rewriting all of these equations which make identifica-

tions far less obvious. For example, if we let $t \to -t$ in Eq. (II-12a), we obtain

$$\phi(-t) = \nu \, \mathrm{Tr}\{\rho(H_0)\, U(-t-i\beta\hbar)\, \vec{\mu}\, U(-t)^{\dagger} \cdot e^{-\frac{iH_0 t}{\hbar}}\, \vec{\mu}\, e^{\frac{iH_0 t}{\hbar}}\}. \quad \text{(II-14)}$$

The equivalence of Eq. (II-12b) and Eq. (II-14) is now not trivial, and it must be obtained from various identities which we will presently derive. An even more subtle problem concerns the following point. One does not obtain a correct expression for $\phi(t+i\beta\hbar)$ by simply replacing t by $(t+i\beta\hbar)$ in the right-hand side of Eq. (II-12a). The reason is, in the $U(t)^{\dagger}$ operator of Eq. (II-12a), the two operations of complex time translation $t \to t+i\beta\hbar$ and of taking the Hermitian adjoint do not commute. We shall show that the correct procedure is to eliminate the adjoint operation, and <u>then</u> to perform the complex time translation.

The basic identity which we shall need is obtained as follows; in Eq. (II-11a) we replace z by $-z^*$ and obtain

$$e^{\frac{iHz^*}{\hbar}} = e^{\frac{iH_0 z^*}{\hbar}}\, U(-z^*) \quad . \quad \text{(II-15)}$$

We now equate Eqs. (II-11b), (II-15) and obtain

$$U(z)^{\dagger} = e^{\frac{iH_0 z^*}{\hbar}}\, U(-z^*)\, e^{-\frac{iH_0 z^*}{\hbar}} \quad . \quad \text{(II-16)}$$

Some useful special cases for real t are

$$U(t)^{\dagger} = e^{\frac{iH_0 t}{\hbar}}\, U(-t)\, e^{-\frac{iH_0 t}{\hbar}} \quad , \quad \text{(II-17a)}$$

$$U(-t)^{\dagger} = e^{-\frac{iH_0 t}{\hbar}} U(t)\, e^{\frac{iH_0 t}{\hbar}} \quad ,(II\text{-}17b)$$

$$U(t) = e^{\frac{iH_0 t}{\hbar}} U(-t)^{\dagger}\, e^{-\frac{iH_0 t}{\hbar}} \quad .(II\text{-}17c)$$

The equivalence of Eqs. (II-12b), (II-14) for $\phi(-t)$ can readily be established by starting from Eq. (II-12b), making use of Eq. (II-16) with $z = t - i\beta\hbar$, inserting Eq. (II-17c) for $U(t)$, and finally using cyclic invariance of the trace expression.

Next we return to the problem of correctly obtaining $\phi(t+i\beta\hbar)$ from $\phi(t)$. Starting from Eq. (II-12a), we make use of Eq. (II-17a) to eliminate the adjoint operation. This converts Eq. (II-12a) to read

$$\phi(t) = \nu\, \mathrm{Tr}\{\rho(H_0)\, U(t-i\beta\hbar)\, \vec{\mu}\, e^{\frac{iH_0 t}{\hbar}} \cdot U(-t)\, \vec{\mu}\, e^{-\frac{iH_0 t}{\hbar}}\} \quad . \quad (II\text{-}18)$$

The complex time translation $t \to t+i\beta\hbar$ then gives

$$\phi(t+i\beta\hbar) = \nu\, \mathrm{Tr}\{\rho(H_0)\, U(t)\, \vec{\mu}$$

$$\cdot\, e^{\frac{iH_0(t+i\beta\hbar)}{\hbar}} U(-t-i\beta\hbar)\, \vec{\mu}\, e^{-\frac{iH_0(t+i\beta\hbar)}{\hbar}}\} \quad . \quad (II\text{-}19)$$

Now inserting Eq. (II-17c) for $U(t)$, Eq. (II-19) simplifies to give our previous expression (II-14) for $\phi(t+i\beta\hbar) = \phi(-t)$.

We have discussed the above points in some detail because we will need to make use of similar manipulations to verify that the FDT is satisfied at later stages of the formulation.

For later purposes, it will also prove convenient to introduce the integral equations for the $U(t)$ operators. With the boundary condition $U(0) = 1$, one obtains the integral equations

$$U(t) = 1 - \frac{i}{\hbar} \int_0^t V(t')\, U(t')\, dt' \qquad ,(II\text{-}20a)$$

$$U(t)^\dagger = 1 + \frac{i}{\hbar} \int_0^t U(t')^\dagger\, V(t')\, dt' \qquad ,(II\text{-}20b)$$

with

$$V(t) = e^{\frac{iH_0 t}{\hbar}}\, V\, e^{-\frac{iH_0 t}{\hbar}} \qquad .(II\text{-}20c)$$

More generally, for complex t, we write

$$U(z) = 1 - \frac{i}{\hbar} \int_0^z V(z')\, U(z')\, dz' \qquad ,(II\text{-}21a)$$

$$\text{with } V(z') = e^{\frac{iH_0 z'}{\hbar}}\, V\, e^{-\frac{iH_0 z'}{\hbar}} \qquad ,(II\text{-}21b)$$

where the integration can be taken over any path in the complex z' plane where the integrand is analytic.

To conclude this section, it is interesting to compare Eq. (II-12a) for $\phi(t)$ with the result one obtains in an analogous theory which does not satisfy the FDT. In such a theory which ignores so-called "back reaction," $\rho(H)$ is approximated by the unperturbed density $\rho(H_0)$, and leads to the result

$$\phi(t) \approx \mathrm{Tr}\{\rho(H_0)\, \vec{\mu}\, U(t)^\dagger\, e^{\frac{iH_0 t}{\hbar}}\, \vec{\mu}\, e^{-\frac{iH_0 t}{\hbar}}\, U(t)\} \qquad . (II\text{-}22)$$

Comparison of Eqs. (II-12a), (II-22) shows that the more complete theory:

(a) Contains the factor $\nu = \frac{Z_0}{Z}$,

(b) Replaces a U(t) factor by $U(t-i\beta\hbar)$,

(c) Contains a rearrangement of the various factors which cannot be eliminated using cyclic invariance of the trace.

Items (a) and (b) above might have been anticipated, however, item (c) is more subtle, and we shall refer to it as a "re-ordering" effect.

III. UNCOUPLED-LINE AND BINARY COLLISION APPROXIMATIONS

In this section we shall make the two approximations discussed in the Introduction, namely the uncoupled-line and binary collision approximations. To facilitate these approximations, it is convenient to separate out the internal states of the radiating molecule in the expression for H_0. Thus we write

$$H_0 = H_{RI}^0 + \tilde{H}_0 \quad , \text{(III-1)}$$

where H_{RI}^0 contains only the internal coordinates of the radiating molecule. Then $\tilde{H}_0$ contains all the rest of the unperturbed Hamiltonian, i.e. the internal coordinates of all perturbers, the translational coordinates of all molecules (including the radiator), and the isotropic interactions between the radiator and perturbers. The unperturbed density matrix then factors as $\rho(H_0) = \rho(H_{RI}^0)\,\rho(\tilde{H}_0)$. The operator $\rho(\tilde{H}_0)$ can also be further factored, however, it is convenient not to use this at present.

We denote the eigenstates of H_{RI}^0 by $|jm\rangle$, where m is the magnetic quantum number, and where j stands for all other quantum numbers necessary to specify the internal state. Now in Eq. (II-12a) we take the trace over $\rho(H_{RI}^0)$ and find

$$\phi(t) = \nu \sum_{j_i j_i' j_f j_f'} \sum_{m_i m_i' m_f m_f'} \rho(\varepsilon_{j_i'}) \, e^{\frac{i}{\hbar}(\varepsilon_{j_f'} - \varepsilon_{j_i'})t}$$

$$\cdot \langle j_i m_i | \vec{\mu} | j_f m_f \rangle \cdot \langle j_f' m_f' | \vec{\mu} | j_i' m_i' \rangle$$

$$\cdot \mathrm{Tr}\{\rho(\tilde{H}_0) \langle j_i' m_i' | U(t - i\beta\hbar) | j_i m_i \rangle \cdot \langle j_f m_f | U(t)^\dagger | j_f' m_f' \rangle\}, \quad \text{(III-2)}$$

$$\text{with } \rho(\varepsilon_{j_i'}) = e^{-\beta\varepsilon_{j_i'}} / \sum_j (2j+1) \, e^{-\beta\varepsilon_j} \quad . \quad \text{(III-3)}$$

In obtaining the above result from Eq. (II-12a), we have used the fact that

$$e^{\frac{iH_0 t}{\hbar}} \vec{\mu} \, e^{-\frac{iH_0 t}{\hbar}} = e^{\frac{iH_{RI}^0 t}{\hbar}} \vec{\mu} \, e^{-\frac{iH_{RI}^0 t}{\hbar}} ,$$

because the remainder of the unperturbed Hamiltonian ($\tilde{H}_0$) commutes with $\vec{\mu}$. It is again interesting to compare Eq. (III-2) with the analogous result derived from Eq. (II-22) which does not satisfy the FDT:

$$\phi(t) = \sum_{j_i j_i' j_f j_f'} \sum_{m_i m_i' m_f m_f'} \rho(\varepsilon_{j_i}) \, e^{\frac{i}{\hbar}(\varepsilon_{j_f'} - \varepsilon_{j_i'})t}$$

$$\cdot \langle j_i m_i | \vec{\mu} | j_f m_f \rangle \cdot \langle j_f' m_f' | \vec{\mu} | j_i' m_i' \rangle$$

$$\cdot \mathrm{Tr}\{\rho(\tilde{H}_0) \langle j_f m_f | U(t)^\dagger | j_f' m_f' \rangle \cdot \langle j_i' m_i' | U(t) | j_i m_i \rangle\} \quad . \quad \text{(III-4)}$$

Comparison of the above equations shows four differences:

(a) The factor of $\nu = Z_0/Z$ in Eq. (III-2),

(b) $U(t) \leftrightarrow U(t - i\beta\hbar)$,

(c) The difference in two statistical factors $\rho(\varepsilon_{j_i'})$ and $\rho(\varepsilon_{j_i})$,

(d) The different order of U relative to $U^\dagger$ in the trace expressions.

Items (c) and (d) above arise from the "reordering" effect discussed previously.

At this point we shall make the uncoupled line approximation, $j_f' = j_f$ and $j_i' = j_i$. In a separate publication, one of the present authors (R. W. D.) will present a somewhat simplified approach which is meant to be applicable only in the far wings. This formulation is carried out in the frequency domain, it satisfies the FDT, and it correctly includes all possible line-coupling effects. We note that the uncoupled line approximation eliminates part of the "reordering" effect discussed above, i.e. $\rho(\varepsilon_{j_i'}) \to \rho(\varepsilon_{j_i})$ in this approximation.

If we now apply the uncoupled line approximation to Eq. (III-2), and then make use of the Wigner-Eckhart theorem for the $\vec{\mu}$ matrix elements, we obtain

$$\phi(t) = \nu \sum_{j_i j_f} \rho(\varepsilon_{j_i})(2j_i+1)|\langle j_i||\mu||j_f\rangle|^2 \cdot e^{\frac{i}{\hbar}(\varepsilon_{j_f}-\varepsilon_{j_i})t}\, C_{if}(t) \quad , \text{(III-5)}$$

where the reduced matrix elements satisfy the symmetry relation

$$(2j_f+1)|\langle j_f||\mu||j_i\rangle|^2 = (2j_i+1)|\langle j_i||\mu||j_f\rangle|^2 \quad , \text{(III-6)}$$

and where $C_{if}(t)$ is a correlation function given by

$$C_{if}(t) = \frac{1}{(2j_i+1)} \sum_{m_i m_i' m_f m_f' m} \cdot (j_f 1 m_f m | j_f 1 j_i m_i)(j_f 1 m_f' m | j_f 1 j_i m_i') \cdot \mathrm{Tr}\{\rho(\tilde{H}_0)\langle j_i m_i'|U(t-i\beta\hbar)|j_i m_i\rangle \cdot \langle j_f m_f|U(t)^\dagger|j_f m_f'\rangle\} \quad . \text{(III-7)}$$

Before proceeding to make the binary collision approximation, it is interesting to note the normalization properties of Eqs. (III-5), (III-7). First we note that $C_{if}(0) \neq 1$. Rather, from Eq. (III-7) we obtain

$$C_{if}(0) = \frac{1}{(2j_i+1)} \sum_{m_i m_i'} \mathrm{Tr}\{\rho(\tilde{H}_0)\langle j_i m_i' | U(-i\beta\hbar) | j_i m_i\rangle\}$$

$$\cdot \sum_{m_f m} (j_f l m_f m | j_f l j_i m_i)(j_f l m_f m | j_f l j_i m_i') \quad . \text{(III-8)}$$

Performing the sum over m_f, m in Eq. (III-8) simply produces a factor of $\delta_{m_i, m_i'}$, and leads to

$$C_{if}(0) = C_i(0) = \frac{1}{2j_i+1} \sum_{m_i} \mathrm{Tr}\{\rho(\tilde{H}_0)\langle j_i m_i | U(-i\beta\hbar) | j_i m_i\rangle\}. \text{(III-9)}$$

Although this does not equal unity, we can write

$$C_{if}(t) = C_i(0)\, \tilde{C}_{if}(t) \quad , \text{(III-10)}$$

or

$$\tilde{C}_{if}(t) = \frac{C_{if}(t)}{C_i(0)} \quad , \text{(III-11)}$$

then $\tilde{C}_{if}(0) = 1$, and we can rewrite Eq. (III-5) as

$$\phi(t) = \sum_{j_i j_f} \tilde{\rho}(\varepsilon_{j_i}) |\langle j_i || \mu || j_f \rangle|^2 \, e^{\frac{i}{\hbar}(\varepsilon_{j_f} - \varepsilon_{j_i})t} \, \tilde{C}_{if}(t), \quad \text{(III-12)}$$

where

$$\tilde{\rho}(\varepsilon_{j_i}) \equiv \nu\, \rho(\varepsilon_{j_i})(2j_i+1)\, C_i(0) \quad . \text{(III-13)}$$

We now show that $\tilde{\rho}(\varepsilon_{j_i})$ is simply a <u>renormalized</u> initial state occupancy, in particular that

$$\sum_{j_i} \tilde{\rho}(\epsilon_{j_i}) = 1 \qquad \text{.(III-14)}$$

To prove this, we combine Eqs. (III-9), (III-13), (III-14) to give

$$\sum_{j_i} \tilde{\rho}(\epsilon_{j_i}) = \nu \sum_{j_i m_i} \rho(\epsilon_{j_i}) \, \mathrm{Tr}\{\rho(\tilde{H}_0)\langle j_i m_i | U(-i\beta\hbar) | j_i m_i \rangle\}$$

$$= \nu \, \mathrm{Tr}\{\rho(H_0) \, U(-i\beta\hbar)\} \qquad \text{,(III-15)}$$

where the trace is now over the <u>complete</u> unperturbed density matrix. However, it may readily be established that

$$\mathrm{Tr}\{\rho(H_0) \, U(-i\beta\hbar)\} = \frac{Z}{Z_0} = \nu^{-1} \qquad \text{,(III-16)}$$

from which the result (III-14) follows immediately.

Now the binary collision approximation to Eq. (III-7) is simply

$$C_{if}(t) = [q_{if}(t)]^{N_P} \qquad \text{,(III-17)}$$

where N_P is the number of perturbers, and with

$$q_{if}(t) = \frac{1}{(2j_i+1)} \sum_{m_i m_i' m_f m_f' m} (j_f l m_f m | j_f l j_i m_i)(j_f l m_f' m | j_f l j_i m_i')$$

$$\cdot \, \mathrm{Tr}\{\rho_S(\tilde{H}_0)\langle j_i m_i' | U_S(t-i\beta\hbar) | j_i m_i \rangle$$

$$\cdot \, \langle j_f m_f | U_S(t)^\dagger | j_f m_f' \rangle\} \qquad \text{.(III-18)}$$

In the expression (III-18), the subscript S on the ρ and U operators denotes that these operators now correspond to a <u>single</u> radiator and perturber.

One next invokes the same argument used by Baranger[5] and others.[22,23] Namely, one assumes that $q_{if}(t)$ has the form

$$q_{if}(t) = [1 + \frac{1}{\Omega} F_{if}(t)] \quad ,(III-19a)$$

$$= [1 + \frac{n_P}{N_P} F_{if}(t)] \quad ,(III-19b)$$

where Ω is the normalization volume, and n_P is the perturber density. Then in the limit of large N_P, Eqs. (III-17), (III-19) yield

$$C_{if}(t) = e^{n_P F_{if}(t)} \quad ,(III-20a)$$

or

$$C_{if}(t) = e^{N_P [q_{if}(t) - 1]} \quad .(III-20b)$$

In order to justify the form in Eqs. (III-19), we can begin by noting from analogy with Eqs. (II-20), (II-21) that the U_S operators in Eq. (III-18) can be written in the form

$$U_S(t)^\dagger = 1 + W_S(t)^\dagger \quad ,(III-21a)$$

$$U_S(t-i\beta\hbar) = 1 + W_S(t-i\beta\hbar) \quad ,(III-21b)$$

where

$$W_S(t) = -\frac{i}{\hbar} \int_0^t V_S(t') U_S(t') dt' \quad ,(III-22a)$$

$$W_S(t)^\dagger = \frac{i}{\hbar} \int_0^t U_S(t')^\dagger V_S(t') dt' \quad ,(III-22b)$$

$$W_S(t-i\beta\hbar) = -\frac{i}{\hbar} \int_0^{t-i\beta\hbar} V_S(z') U_S(z') dz' \quad .(III-22c)$$

Then in Eq. (III-18), the term in the product of the U's corresponding to unity may readily be shown to sum to unity,

which justifies the first term in Eq. (III-19a). The volume dependence of the second term in Eq. (III-19a) will be established at a later stage.

It is important, after having made the uncoupled line and binary collision approximations, to be able to demonstrate that the FDT is still rigorously satisfied. The proof that this is, indeed, the case is given in the Appendix. Briefly, the proof consists of first showing that the FDT is satisfied provided

$$C_{fi}(-t) = C_{if}(t+i\beta\hbar) \quad , \text{(III-23)}$$

(note the exchange of indices i, f). In our binary collision approximation, (III-20b), the condition (III-23) is clearly satisfied provided we can show

$$q_{fi}(-t) = q_{if}(t+i\beta\hbar) \quad . \text{(III-24)}$$

The details of this proof are carried out in the Appendix. We also remark, in the uncoupled-line and binary collision approximations, that the reality condition, Eq. (II-7), is satisfied provided $C_{if}(t)^* = C_{if}(-t)$, i.e. if $q_{if}(t)^* = q_{if}(-t)$. This relation can be proven using manipulations similar to those found in the Appendix.

Returning to Eq. (III-18), we can make use of Eqs. (III-22) to write

$$[q_{if}(t)-1] = \frac{1}{(2j_i+1)} \sum_{m_i m_i' m_f m_f' m} (j_f l m_f m | j_f l j_i m_i)(j_f l m_f' m | j_f l j_i m_i')$$

$$\cdot \{\mathrm{Tr}\{\rho_S(\tilde{H}_0)\langle j_i m_i' | W_S(t-i\beta\hbar) | j_i m_i\rangle\} \delta_{m_f', m_f}$$

$$+ \mathrm{Tr}\{\rho_S(\tilde{H}_0)\langle j_f m_f | W_S(t)^\dagger | j_f m_f'\rangle\} \delta_{m_i' m_i}$$

$$+ \mathrm{Tr}\{\rho_S(\tilde{H}_0)\langle j_i m_i' | W_S(t-i\beta\hbar) | j_i m_i\rangle \cdot \langle j_f m_f | W_S(t)^\dagger | j_f m_f'\rangle\}\}. \quad \text{(III-25)}$$

Once again, we can compare this to the result one obtains from Eqs. (II-22), (III-4) which do not satisfy the FDT. In the simpler theory, $W_S(t-i\beta\hbar)$ is replaced by $W_S(t)$ in the first and third terms of Eq. (III-25). In addition, in the third term of Eq. (III-25), the order of the initial and final state matrix elements is reversed in the simpler theory. This is the only remaining "reordering" effect.

We also remark that the first two terms in Eq. (III-25) roughly correspond to $S(b)_{outer}$ in Anderson theory,[3,24] while the last term corresponds to Anderson's $S(b)_{inner}$. In graphical perturbation theory[25] the two types of terms correspond to self-energy and vertex corrections, respectively.

IV. INVESTIGATION OF TIME-DEPENDENCE IN LOW-ORDER PERTURBATION THEORY

It is clear, since the U_S operators in Eqs. (III-22) satisfy integral equations, that it will be extremely difficult to rigorously treat the anisotropic interaction V to an arbitrary order in perturbation theory. In this section we will therefore confine our discussion of the theory to second order. However, as we shall point out, only the quantitative details are altered if the theory is carried to third or higher order. Moreover, we also point out that the present theory satisfies the FDT order-by-order in perturbation theory.

In this section, in order to provide a more simplified account, we shall treat the internal states of both the radiator and perturber as non-degenerate, i.e. we shall ignore the (2j+1)-fold degeneracy in the m indices. This also means that we shall suppress the Clebsch-Gordan coefficients and the m summations in Eqs. (III-18), (III-25), and shall set factors of (2j+1) equal to unity. These details can easily be retained, but are important only for numerical calculations, which will not be attempted in this paper. As a final simplification in notation, we shall also drop the subscript S on the ρ_S, U_S, W_S, V_S operators which appear in Eqs. (III-18)-(III-25), understanding that these operators now refer to a single radiator and perturber.

We shall begin by considering the second term in Eq. (III-25), which we now simplify to read

$$K_f(t) = \mathrm{Tr}\ \{\rho(H_0)\ \langle j_f|W(t)^\dagger|j_f\rangle\} \quad . \quad \text{(IV-1)}$$

This term enters in an identical fashion in both the theory which satisfies the FDT, and the one which does not. However, before considering this term in detail, we briefly remark on the other two terms of Eq. (III-25), which we also simplify as

$$K_i(t) = \mathrm{Tr}\ \{\rho(\tilde{H}_0)\ \langle j_i|W(t-i\beta\hbar)|j_i\rangle\} \quad , \quad \text{(IV-2)}$$

$$K_{if}(t) = \mathrm{Tr}\ \{\rho(\tilde{H}_0)\langle j_i|W(t-i\beta\hbar)|j_i\rangle\cdot\langle j_f|W(t)^\dagger|j_f\rangle\} \quad . \quad \text{(IV-3)}$$

Concerning Eq. (IV-2), at large times ($|t| >> \beta\hbar$) this term can be approximated by

$$K_i(t) = \mathrm{Tr}\{\rho(\tilde{H}_0)\ \langle j_i|W(t)|j_i\rangle\} \quad , \quad \text{(IV-4)}$$

and the discussion in this regime is essentially identical to that which we present for $K_f(t)$ at large t. At very small times, $K_i(t)$ approaches the finite constant

$$K_i(0) = \mathrm{Tr}\{\rho(\tilde{H}_0)\ \langle j_i|W(-i\beta\hbar)|f_i\rangle\} \quad , \quad \text{(IV-5)}$$

and, as discussed in Section III, leads to a renormalization of the initial state occupancy. The discussion of Eq. (IV-3) is somewhat more complicated, and this will be given separately.

In order to perform the trace in Eq. (IV-1), we need the resolution of the identity operator in terms of the product states of H_0. This can be written

$$\sum_{j_f' J' \vec{k}'} |j_f' J' \psi_{\vec{k}'}\rangle\langle j_f' J' \psi_{\vec{k}'}| = 1 \quad , \quad \text{(IV-6)}$$

with $|j_f' J' \psi_{\vec{k}'}'\rangle = |j_f'\rangle |J'\rangle |\psi_{\vec{k}'}'\rangle$, (IV-7)

where $|j_f'\rangle$ denotes an internal state of the radiator, $|J'\rangle$ denotes an internal state of the perturber, and where $|\psi_{\vec{k}'}'\rangle$ is an eigenstate of the Hamiltonian

$$H_{ISO}^0 = -\frac{\hbar^2 \nabla^2}{2m} + V_0(r) \quad . \quad \text{(IV-8)}$$

In Eq. (IV-8), $\nabla^2 = \nabla_{\vec{r}}^2$, with $\vec{r} = \vec{r}_1 - \vec{r}_2$ the relative coordinate, $m = m_1 m_2/(m_1+m_2)$ the reduced mass, and $V_0(r)$ is the isotropic pair potential. Since $\vec{\mu}$, V_0, V do not depend on the center of mass coordinate, $\vec{R}$, of the pair, it can be seen that the translational motion of the center of mass plays no role in the subsequent theory. We thus have

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + V_0(r)\right] |\psi_{\vec{k}}\rangle = \varepsilon_{\vec{k}} |\psi_{\vec{k}}\rangle \quad . \quad \text{(IV-9)}$$

For unbound states $|\psi_{\vec{k}}\rangle$ can be taken as any suitably normalized set of continuum eigenstates, and $\varepsilon_{\vec{k}} = \hbar^2 k^2/2m$. However, if $V_0(r)$ leads to bound states, sums over $|\psi_{\vec{k}}\rangle$ implicitly contain a sum over the bound states. The unperturbed energy associated with a state $|j_f J \psi_{\vec{k}}\rangle$ can then be written

$$\varepsilon_{j_f J \vec{k}} = \varepsilon_{j_f} + \varepsilon_J + \varepsilon_{\vec{k}} \quad . \quad \text{(IV-10)}$$

If we now evaluate Eq. (IV-1) in first order perturbation theory using Eq. (III-22b), we obtain

$$K_f^{(1)}(t) = \frac{it}{\hbar} \sum_{\vec{k}J} \rho(\varepsilon_{\vec{k}})\, \rho(\varepsilon_J) \cdot \langle j_f J \psi_{\vec{k}} | V | j_f J \psi_{\vec{k}} \rangle \quad , \quad \text{(IV-11)}$$

with

$$\rho(\varepsilon_{\vec{k}}) \equiv e^{-\beta\varepsilon_{\vec{k}}} / \sum_{\vec{k}''} e^{-\beta\varepsilon_{\vec{k}''}} \quad . \text{(IV-12)}$$

The expression (IV-11) is seen to be a linear function of t without any approximations. We note, however, that $K_f^{(1)}(t)$ is pure imaginary, and therefore it contributes a phase shift, rather than damping, to the autocorrelation function $C_{if}(t)$. It can also be shown, for multipole interactions, that $K_f^{(1)}(t)$ vanishes when a sum over magnetic quantum numbers is performed[25] (which is suppressed here). In what follows, we shall therefore neglect these first order phase shifts.

We next evaluate $K_f(t)$ in second order perturbation theory, and find

$$K_f^{(2)}(t) = -\frac{1}{\hbar^2} \sum_{J\vec{k}} \rho(\varepsilon_J)\, \rho(\varepsilon_{\vec{k}}) \cdot \sum_{j_f' J' \vec{k}'} |\langle\alpha|V|\beta\rangle|^2 \, f(t) \quad , \text{(IV-13)}$$

where, for simplicity, $|\alpha\rangle \equiv |j_f J \psi_{\vec{k}}\rangle$, $|\beta\rangle \equiv |j_f, J' \psi_{\vec{k}'}\rangle$, and where

$$f(t) = -\frac{i\hbar}{(\varepsilon_\alpha - \varepsilon_\beta)} \left\{ t - i\hbar \frac{[e^{\frac{i}{\hbar}(\varepsilon_\alpha - \varepsilon_\beta)t} - 1]}{(\varepsilon_\alpha - \varepsilon_\beta)} \right\} \quad . \text{(IV-14)}$$

An alternative and useful form for the f(t) function is

$$f(t) = \frac{1}{\omega_{\alpha\beta}^2} [1 - \cos(\omega_{\alpha\beta} t)] - \frac{i}{\omega_{\alpha\beta}^2} [\omega_{\alpha\beta} t - \sin(\omega_{\alpha\beta} t)] \quad , \text{(IV-15)}$$

where, $\omega_{\alpha\beta} \equiv (\varepsilon_\alpha - \varepsilon_\beta)/\hbar$. In this second form it is immediately clear that the real part of f(t) is an even function of t, while the imaginary part is odd. Also from Eqs. (IV-13),

(IV-15), we see that the real part of $K_f^{(2)}(t)$ is always negative (gives damping).

The time dependence of $K_f^{(2)}(t)$ for long and short times can now be deduced from a study of the f(t) function. First we note that f(t) is a perfectly well-behaved function when $(\varepsilon_\alpha - \varepsilon_\beta) \to 0$. By expanding the exponential in Eq. (IV-14), we find

$$f(t) \simeq \frac{1}{2} t^2 \text{ as } (\varepsilon_\alpha - \varepsilon_\beta) \to 0 \quad . \text{ (IV-16)}$$

Furthermore it is clear that the above result is precisely what we get in the small time limit $t \to 0$. Hence, for short times,

$$K_f^{(2)}(t) \simeq - \frac{t^2}{2\hbar^2} \sum_{J\vec{k}} \rho(\varepsilon_J)\, \rho(\varepsilon_{\vec{k}}) \cdot \sum_{j_f' J' \vec{k}'} |\langle j_f J \psi_{\vec{k}} | V | j_f', J' \psi_{\vec{k}'} \rangle|^2 . \quad \text{(IV-17)}$$

Thus as $t \to 0$, $K^{(2)}(t)$ is a real, quadratic function of time, and from Eq. (III-20b), it leads to a correlation function of Gaussian form.

In order to examine the long time behavior, we make use of the identities[26]

$$\lim_{|t| \to \infty} \frac{[1-\cos(\omega_{\alpha\beta} t)]}{\omega_{\alpha\beta}^2} = \pi\, \delta(\omega_{\alpha\beta}) |t| \quad , \text{ (IV-18)}$$

$$\lim_{|t| \to \infty} \frac{1}{\omega_{\alpha\beta}^2} [\omega_{\alpha\beta} t - \sin(\omega_{\alpha\beta} t)] = t\, \frac{Pr}{\omega_{\alpha\beta}} \quad . \text{ (IV-19)}$$

Hence the long time limit of $K_f^{(2)}(t)$ is given by

$$K_f^{(2)}(t) = -\frac{|t|}{\hbar} \sum_{J\vec{k}} \sum_{j_f'J'\vec{k}'} \rho(\varepsilon_J)\rho(\varepsilon_{\vec{k}})$$

$$\cdot |\langle j_f J\psi_{\vec{k}}|V|j_f'J'\psi_{\vec{k}'}\rangle|^2 \pi \delta(\varepsilon_{j_f J\vec{k}} - \varepsilon_{j_f'J'\vec{k}'})$$

$$- \frac{it}{\hbar} \sum_{J\vec{k}} \sum_{j_f'J'\vec{k}'} \rho(\varepsilon_J)\, \rho(\varepsilon_{\vec{k}})$$

$$\cdot |\langle j_f J\psi_{\vec{k}}|V|j_f'J'\psi_{\vec{k}'}\rangle|^2 \frac{Pr}{(\varepsilon_{j_f J\vec{k}} - \varepsilon_{j_f'J'\vec{k}'})} \quad . \text{(IV-20)}$$

The above result is identical to the impact approximation[25,27] in second order perturbation theory. The appearance of $|t|$ in the damping term is also familiar in the impact theory. If one assumes Eq. (IV-20) to be valid for all times, including the neighborhood of $t = 0$, the factor $|t|$ leads to singularities in the derivatives of $C_{if}(t)$ at $t = 0$. This immediately implies that the higher order moments[17] of the lineshape function (the Fourier transform of $C_{if}(t)$) do not exist in the impact theory. As we have seen from Eq. (IV-17), the correct damping of $C_{if}(t)$ at small t is Gaussian, which implies that all moments of the lineshape function are well-defined and finite. In the frequency domain, these results imply that the extreme far wings must decay in some "exponential" fashion, rather than the simple $(\omega-\omega_{if})^{-2}$ decay predicted by the impact theory.

For intermediate times, it is clear that the time dependence of $K_f^{(2)}(t)$ is complicated, and it will probably need to be extracted numerically. A rough criterion for the inter-

mediate time region is $\langle\omega_{\alpha\beta}\rangle\, t \simeq 1$, where $\langle\omega_{\alpha\beta}\rangle$ is some average energy difference. For a situation in which $\hbar\langle\omega_{\alpha\beta}\rangle \simeq k_B T$, we estimate the transition region to occur at times of order $t \simeq \hbar/k_B T = \beta\hbar = 2.6 \times 10^{-14}$ sec, for T = 296K. It is then clear that this is precisely the range where the difference between $W(t-i\beta\hbar)$ and $W(t)$ begins to be important in the $K_i(t)$ term.

Before going on, we remark that the long time behavior of the term $K_i^{(2)}(t)$ (with $W(t-i\beta\hbar) \simeq W(t)$) can be obtained from Eq. (IV-20) with the substitutions $j_f \to j_i$, $j_f' \to j_i'$, and with the imaginary term in Eq. (IV-20) changing sign. This implies that the real parts of $K_i^{(2)}(t)$ and $K_f^{(2)}(t)$ add, while the imaginary parts subtract. This is also familiar from the impact theory.

A second item that can be disposed of at this point is justification of the normalization volume dependence in the second term of Eq. (III-19a), i.e. we now show that $K_f^{(2)}(t)$, as given by Eqs. (IV-17), (IV-20), is correctly proportional to $1/\Omega$. To see this we rewrite Eq. (IV-12) as

$$\rho(\varepsilon_{\vec{k}}) = \frac{1}{\Omega} e^{-\beta\varepsilon_{\vec{k}}} / \left(\frac{1}{\Omega} \sum_{\vec{k}''} e^{-\beta\varepsilon_{\vec{k}''}}\right) \qquad \text{. (IV-21)}$$

In the limit of large Ω, $\frac{1}{\Omega}\sum_{\vec{k}''} \to \frac{1}{(2\pi)^3}\int d^3\vec{k}''$, and the remaining factor of $\frac{1}{\Omega}$ in Eq. (IV-21) turns out to give the expected $\frac{1}{\Omega}$ volume dependence of $K_f^{(2)}(t)$. To complete the proof, we note that if $|\psi_{\vec{k}}\rangle$ is a continuum wavefunction, it will contain

a normalization factor of $\frac{1}{\sqrt{\Omega}}$, while bound state $|\psi_S'\rangle$ are normalized independent of Ω. Then in Eqs. (IV-17), (IV-20), if $|\psi_{\vec{k}}\rangle$ and $|\psi_{\vec{k}'}\rangle$ are both continuum states, the square of the matrix element yields a factor $1/\Omega^2$. This is just what is needed to turn the $\vec{k}$, $\vec{k}'$ sums into integrals. Likewise one sees that the volume dependence is correct for bound → free, and bound → bound matrix elements.

We next consider the more complicated quantity $K_{if}(t)$ as given by Eq. (IV-3). It is also interesting to compare this with a quantity

$$\tilde{K}_{if}(t) = \mathrm{Tr}\{\rho(\tilde{H}_0)\langle j_f|W(t)^\dagger|j_f\rangle\cdot\langle j_i|W(t)|j_i\rangle\} \quad , \text{(IV-22)}$$

which obtains in the analogous theory where the FDT is not satisfied. In comparing Eqs. (IV-3), (IV-22) we note that a "reordering" effect remains. However, a careful examination of these equations (including magnetic quantum numbers suppressed here) shows that, to second order, the "reordering" effect plays no role, and only the difference $W(t) \to W(t-i\beta\hbar)$ is important. We also remark that if one confines the analysis to second order perturbation theory, there are a number of interesting cases where K_{if} and $\tilde{K}_{if}$ vanish. This happens for linear and asymmetric rotor (radiating) molecules for the case of dipole-dipole or dipole-quadrupole interactions, because one obtains <u>diagonal</u> reduced matrix elements of the radiator's dipole moment operator. These results are also familiar from Anderson theory,[3,24] i.e. $S(b)_{inner}$ makes no contribution in such cases.

We note from Eqs. (IV-3), (IV-22) that $K_{if}(t)$ and $\tilde{K}_{if}(t)$ are already at least of second order in V. Then to second order, evaluation of the formulas for large t gives

$$K_{if}^{(2)}(t) \simeq \tilde{K}_{if}^{(2)}(t) = \frac{2|t|}{\hbar} \sum_{J\vec{k}} \sum_{J'\vec{k}'} \rho(\epsilon_J)\, \rho(\epsilon_{\vec{k}})$$

$$\langle j_i J\psi_{\vec{k}}|V|j_i J'\psi_{\vec{k}'}\rangle\langle j_f J'\psi_{\vec{k}'}|V|j_f J\psi_{\vec{k}}\rangle$$

$$\cdot\, \pi\, \delta(\epsilon_{J\vec{k}} - \epsilon_{J'\vec{k}'}) \qquad . \text{(IV-23)}$$

This is, again, the impact result, and $K_{if}^{(2)}(t)$ <u>subtracts</u> from the damping given by the $K_i^{(2)}(t)$ and $K_f^{(2)}(t)$ terms.

Next for short times, Eq. (IV-22) evaluates to give

$$\tilde{K}_{if}^{(2)}(t) \simeq \frac{t^2}{\hbar^2} \sum_{J\vec{k}} \sum_{J'\vec{k}'} \rho(\epsilon_J)\, \rho(\epsilon_{\vec{k}})$$

$$\cdot \langle j_i J\psi_{\vec{k}}|V|j_i J'\psi_{\vec{k}'}\rangle\langle j_f J'\psi_{\vec{k}'}|V|j_f J\psi_{\vec{k}}\rangle \qquad . \text{(IV-24)}$$

This term is quadratic in time and subtracts from the damping given by $K_f^{(2)}(t)$. However, at very short times we should consider, instead of $\tilde{K}_{if}(t)$, the function $K_{if}(t)$ which satisfies the FDT. Its small time limit is

$$K_{if}^{(2)}(t) = \frac{t^2}{2\hbar^2} \sum_{J\vec{k}} \sum_{J'\vec{k}'} \rho(\epsilon_J)\, \rho(\epsilon_{\vec{k}}) \cdot [e^{\beta\hbar(\omega_{J\vec{k}} - \omega_{J'\vec{k}'})} + 1]$$

$$\cdot \langle j_i J\psi_{\vec{k}}|V|j_i J'\psi_{\vec{k}'}\rangle\langle j_f J'\psi_{\vec{k}'}|V|j_f J\psi_{\vec{k}}\rangle$$

$$- \frac{it}{\hbar^2} \sum_{J\vec{k}} \sum_{J'\vec{k}'} \rho(\epsilon_J)\, \rho(\epsilon_{\vec{k}})$$

$$\cdot \frac{1}{\omega_{J\vec{k}} - \omega_{J'\vec{k}'}} [e^{\beta\hbar(\omega_{J\vec{k}} - \omega_{J'\vec{k}'})} - 1]$$

$$\cdot \langle j_i J\psi_{\vec{k}}|V|j_i J'\psi_{\vec{k}'}\rangle\langle j_f J'\psi_{\vec{k}'}|V|j_f J\psi_{\vec{k}}\rangle \qquad . \text{(IV-25)}$$

We note, although $K_{if}^{(2)}(t)$ contains a term linear in t, that this term corresponds to a phase shift, rather than damping. Hence we again find that the damping occurs quadratically at small t. Finally, for completeness, we quote the general results for $K_{if}^{(2)}(t)$ and $K_{i}^{(2)}(t)$ in second order perturbation theory;

$$K_{if}^{(2)}(t) = - \sum_{J\vec{k}} \sum_{J'\vec{k}'} \rho(\varepsilon_J)\rho(\varepsilon_{\vec{k}}) \cdot \langle j_i J\psi_{\vec{k}}|V|j_i J'\psi_{\vec{k}'}\rangle\langle j_f J'\psi_{\vec{k}'}|V|j_f J\psi_{\vec{k}}\rangle$$

$$\cdot \frac{[e^{\frac{i}{\hbar}(\varepsilon_{J'\vec{k}'}-\varepsilon_{J\vec{k}})t} - 1]}{(\varepsilon_{J'\vec{k}'}-\varepsilon_{J\vec{k}})}$$

$$\cdot \frac{[e^{\frac{i}{\hbar}(\varepsilon_{J\vec{k}}-\varepsilon_{J'\vec{k}'})(t-i\beta\hbar)} - 1]}{(\varepsilon_{J\vec{k}}-\varepsilon_{J'\vec{k}'})} \quad , \text{(IV-26)}$$

The long time ($|t| >> \beta\hbar$) limit (Eq. (IV-23) is obtained from this formula by again using the identity (IV-18). The short time limit leads directly to Eq. (IV-25). For $K_{i}^{(2)}(t)$, we find

$$K_{i}^{(2)}(t) = - \frac{1}{\hbar^2} \sum_{J\vec{k}} \rho(\varepsilon_J)\rho(\varepsilon_{\vec{k}}) \sum_{j_i' J'\vec{k}'} |\langle j_i J\psi_{\vec{k}}|V|j_i' J'\psi_{\vec{k}'}\rangle|^2 \tilde{f}(t) \quad , \text{(IV-27)}$$

with

$$\tilde{f}(t) = \frac{i\hbar}{(\varepsilon_\alpha-\varepsilon_\beta)} \{(t-i\beta\hbar) + i\hbar \frac{[e^{\frac{i}{\hbar}(\varepsilon_\alpha-\varepsilon_\beta)(t-i\beta\hbar)} - 1]}{(\varepsilon_\alpha-\varepsilon_\beta)} \quad , \text{(IV-28)}$$

and where $\varepsilon_\alpha \equiv \varepsilon_{j_i J\vec{k}}$, $\varepsilon_\beta \equiv \varepsilon_{j_i' J'\vec{k}'}$. It is not difficult to explicitly show that our second-order result for $[q_{if}(t) - 1]$, as obtained from Eqs. (IV-13), (IV-27), (IV-26), satisfies the FDT, and it appears that the FDT is satisfied order-by-order in perturbation theory.

V. DISCUSSION

Within the binary collision and uncoupled-line approximations, we have derived an expression for the dipole autocorrelation function which rigorously satisfies the Fluctuation Dissipation Theorem. We have shown how these results go into the impact theory at large times. For short times we have found that $C_{if}(t)$ is damped in a Gaussian fashion. Although our analysis in Section IV was confined to second order perturbation theory in the anisotropic interaction, by going to third order we can easily convince ourselves that the above behavior is completely general, and only the details are altered in higher order perturbation theory. These results imply that the lineshape function in the frequency domain must decay in some "exponential" fashion sufficiently far in the wings.

Although we have refrained from labeling the present formulation as a "unified" theory, we believe that it qualifies as such. One reason that we have avoided the above label is that most authors of "unified" treatments are content to show that their formulation goes into the impact limit at large times, and for small times takes the form of the quasi-static or statistical theory.[28-30]

We have shown that the present theory, indeed, does reduce to the impact approximation at large times. However, it is not clear that the small time limit of the present formula-

tion has very much in common with the standard statistical theory.

One problem in establishing such a connection is that most formulations of the statistical theory are what Smith, et al[31] have termed "scalar" theories; i.e. at some convenient stage, the dependence of the potential on the internal states is ignored, except possibly for a constant which may depend on the various vibrational or electronic bands of interest. In our present formulation, if the anisotropic interaction vanishes, $C_{if}(t) = 1$, and there is neither broadening nor shift of the spectral transition. This result has also been proven by Baranger[5] in a slightly different context, within the impact approximation.

Another aspect of the simple statistical theory also deserves comment. In a very terse, but highly illuminating paper, Yakimets[32] has applied a "scalar" statistical theory to far wing pressure broadening. By invoking the high energy approximation,[33] and using the method of stationary phase, Yakimets derives a result for the far wing lineshape function for potentials of the form (σ/r^n). Similar results have been obtained by Holstein[34] and others. The result for the (pseudo) dipole-dipole case ($n = 3$) is that the far wing decays as $(\omega-\omega_{fi})^{-2}$, precisely the same dependence as the impact approximation would give. Although the above result may have validity somewhere in the wings, our present formulation shows that it cannot possibly be correct in the <u>extreme</u> far wings, which

must be "exponential." It is clear that theorists such as Yakimets and Holstein are well aware of the above limitations, however, there appears to be a misconception among some workers that the statistical theory is applicable in the extreme wing region.

Finally, although our formulation has been completely quantum mechanical, this does not appear to preclude the use of semiclassical methods. In particular, the eigenstates $|\psi_{\vec{k}}\rangle$ of the isotropic Hamiltonian (IV-8) might be chosen to be time-independent WKB wavefunctions. We hope to explore this and other computational possibilities in a future publication.

APPENDIX

PROOF THAT THE FDT IS SATISFIED IN THE BINARY COLLISION AND UNCOUPLED-LINE APPROXIMATIONS

The first step in the proof is to show, for an uncoupled-line approximation of the form Eq. (III-5), that a sufficient condition for the FDT to be satisfied is

$$C_{fi}(-t) = C_{if}(t+i\beta\hbar) \quad . \quad \text{(A-1)}$$

The above relation applies to any uncoupled-line approximation, and is not limited to the binary collision case.

Now, starting from Eq. (III-5), we have

$$\phi(-t) = \nu \sum_{j_i j_f} \rho(\varepsilon_{j_i})(2j_i+1)|\langle j_i||\mu||j_f\rangle|^2 \; e^{-\frac{i}{\hbar}(\varepsilon_{j_f}-\varepsilon_{j_i})t} \; C_{if}(-t) \quad . \quad \text{(A-2)}$$

We next change names of dummy variables $i \rightleftarrows f$, and make use of the symmetry relation (III-6) for the reduced matrix elements. This gives,

$$\phi(-t) = \nu \sum_{j_i j_f} \rho(\varepsilon_{j_f})(2j_i+1)|\langle j_i||\mu||j_f\rangle|^2 \cdot e^{\frac{i}{\hbar}(\varepsilon_{j_f}-\varepsilon_{j_i})t} \; C_{fi}(-t) \quad . \quad \text{(A-3)}$$

Retaining this result, we next obtain, from Eq. (III-5), the result,

$$\phi(t+i\beta\hbar) = \nu \sum_{j_i j_f} \rho(\varepsilon_{j_i})(2j_i+1)|\langle j_i||u||j_f\rangle|^2$$

$$\cdot\, e^{\frac{i}{\hbar}(\varepsilon_{j_f}-\varepsilon_{j_i})(t+i\beta\hbar)} C_{if}(t+i\beta\hbar) \quad . \quad \text{(A-4)}$$

From Eq. (III-3), we note that

$$\rho(\varepsilon_{j_i})\, e^{-\beta(\varepsilon_{j_f}-\varepsilon_{j_i})} = \rho(\varepsilon_{j_f}) \quad . \quad \text{(A-5)}$$

This gives

$$\phi(t+i\beta\hbar) = \nu \sum_{j_i j_f} \rho(\varepsilon_{j_f})(2j_i+1)|\langle j_i||u||j_f\rangle|^2$$

$$\cdot\, e^{\frac{i}{\hbar}(\varepsilon_{j_f}-\varepsilon_{j_i})t} C_{if}(t+i\beta\hbar) \quad . \quad \text{(A-6)}$$

Comparing Eqs. (A-3), (A-6) we see that a sufficient condition that the FDT theorem (Eq. (II-6)) be satisfied is just Eq. (A-1). It is then clear, in our binary collision approximation (III-20b), that (A-1) is satisfied provided we can show

$$q_{fi}(-t) = q_{if}(t+i\beta\hbar) \quad . \quad \text{(A-7)}$$

To prove the above result, we start from Eq. (III-18) and construct $q_{fi}(-t)$. To carry this out, we let $t \to -t$, $j_i \overset{+}{\to} j_f$, and it is also convenient to make the following changes in the dummy m-summation indices:

$$m_f \to m_i'$$

$$m_f' \to m_i$$

$$m_i' \to m_f$$

$$m_i \to m_f'$$

$$m \to -m \quad . \quad \text{(A-8)}$$

This leads to the result

$$q_{fi}(-t) = \frac{1}{2j_f+1} \sum_{m_i m_i' m_f m_f' m} (j_i l m_i' - m | j_i l j_f m_f')(j_i l m_i - m | j_i l j_f m_f)$$

$$\cdot \mathrm{Tr}\{\rho_S(\tilde{H}_0)\langle j_f m_f | U_S(-t-i\beta\hbar) | j_f m_f'\rangle$$

$$\cdot \langle j_i m_i | U_S(-t)^\dagger | j_i m_i'\rangle\} \quad . \quad \text{(A-9)}$$

We next make use of the symmetry properties[24,35] of Clebsch-Gordan coefficients to obtain the identity

$$(j_i l m_i' - m | j_i l j_f m_f')(j_i l m_i - m | j_i l j_f m_f)$$

$$= \frac{(2j_f+1)}{(2j_i+1)} (j_f l m_f m | j_f l j_i m_i) \cdot (j_f l m_f' m | j_f l j_i m_i') \quad . \quad \text{(A-10)}$$

Upon inserting this result into Eq. (A-9), we obtain

$$q_{fi}(-t) = \frac{1}{(2j_i+1)} \sum_{m_i m_i' m_f m_f' m} (j_f l m_f m | j_f l j_i m_i)(j_f l m_f' m | j_f l j_i m_i')$$

$$\cdot \mathrm{Tr}\{\rho_S(\tilde{H}_0)\langle j_f m_f | U_S(-t-i\beta\hbar) | j_f m_f'\rangle$$

$$\cdot \langle j_i m_i' | U_S(-t)^\dagger | j_i m_i\rangle\} \quad . \quad \text{(A-11)}$$

Retaining this result, we now want to compute $q_{if}(t+i\beta\hbar)$, starting from Eq. (III-18) for $q_{if}(t)$. Recalling our discussion in Section II, we have to be careful in performing this exercise. In particular, we have to eliminate the adjoint operation in Eq. (III-18), before making the complex time translation $t \to t + i\beta\hbar$. Thus we make use of Eq. (II-17a) to write

$$\langle j_f m_f | U_S(t)^\dagger | j_f m_f' \rangle$$

$$= \langle j_f m_f | e^{\frac{iH_0 t}{\hbar}} U_S(-t) e^{-\frac{iH_0 t}{\hbar}} | j_f m_f' \rangle$$

$$= e^{\frac{i\tilde{H}_0 t}{\hbar}} \langle j_f m_f | U_S(-t) | j_f m_f' \rangle e^{-\frac{i\tilde{H}_0 t}{\hbar}} \quad . \quad \text{(A-12)}$$

Now inserting (A-12) into Eq. (III-18), and then letting $t \to t+i\beta\hbar$, we find

$$q_{if}(t+i\beta\hbar) = \frac{1}{(2j_i+1)} \sum_{m_i m_i' m_f m_f' m} (j_f l m_f m | j_f l j_i m_i)(j_f l m_f' m | j_f l j_i m_i')$$

$$\cdot \mathrm{Tr}\{\rho_S(\tilde{H}_0) \langle j_i m_i' | U_S(t) | j_i m_i \rangle$$

$$\cdot e^{\frac{i\tilde{H}_0}{\hbar}(t+i\beta\hbar)} \langle j_f m_f | U_S(-t-i\beta\hbar) | j_f m_f' \rangle$$

$$\cdot e^{-\frac{i\tilde{H}_0}{\hbar}(t+i\beta\hbar)}\} \quad . \quad \text{(A-13)}$$

Application of cyclic invariance gives

$$\mathrm{Tr}\{\quad\} = \mathrm{Tr}\{e^{-\frac{i\tilde{H}_0 t}{\hbar}} \langle j_i m_i' | U_S(t) | j_i m_i \rangle e^{\frac{i\tilde{H}_0 t}{\hbar}}$$

$$\cdot \rho_S(\tilde{H}_0) \langle j_f m_f | U_S(-t-i\beta\hbar) | j_f m_f' \rangle\} \quad . \quad \text{(A-14)}$$

We then note that

$$e^{-\frac{i\tilde{H}_0 t}{\hbar}} \langle j_i m_i' | U_S(t) | j_i m_i \rangle \, e^{\frac{i\tilde{H}_0 t}{\hbar}}$$

$$= \langle j_i m_i' | e^{-\frac{iH_0 t}{\hbar}} U_S(t) \, e^{\frac{iH_0 t}{\hbar}} | j_i m_i \rangle$$

$$= \langle j_i m_i' | U_S(-t)^\dagger | j_i m_i \rangle \quad , \quad \text{(A-15)}$$

where we have made use of Eq. (II-17b) in the last step.

Inserting (A-15) into (A-14) yields

$$\mathrm{Tr}\ \{\quad\} =$$

$$\mathrm{Tr}\ \{\langle j_i m_i' | U_S(-t)^\dagger | j_i m_i \rangle\ \rho_S(\tilde{H}_0) \langle j_f m_f | U_S(-t-i\beta\hbar) | j_f m_f' \rangle\}$$

$$= \mathrm{Tr}\ \{\rho_S(\tilde{H}_0) \langle j_f m_f | U_S(-t-i\beta\hbar) | j_f m_f' \rangle$$

$$\cdot \langle j_i m_i' | U_S(-t)^\dagger | j_i m_i \rangle\} \quad . \quad \text{(A-16)}$$

Upon inserting (A-16) into (A-13), we find

$$q_{if}(t+i\beta\hbar) = \frac{1}{(2j_i+1)} \sum_{m_i m_i' m_f m_f' m} (j_f l m_f m | j_f l j_i m_i)(j_f l m_f' m | j_f l j_i m_i')$$

$$\cdot \mathrm{Tr}\{\rho_S(\tilde{H}_0) \langle j_f m_f | U_S(-t-i\beta\hbar) | j_f m_f' \rangle$$

$$\cdot \langle j_i m_i' | U_S(-t)^\dagger | j_i m_i \rangle\} \quad . \quad \text{(A-17)}$$

The above result is seen to be identical to Eq. (A-11) for $q_{fi}(-t)$. This completes the proof.

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